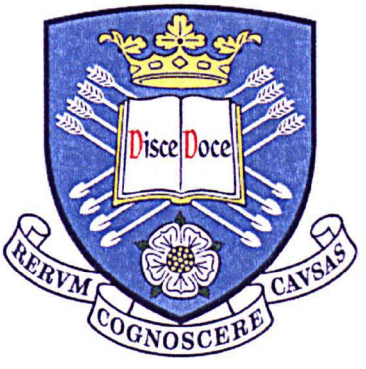
ENERGY RECOVERY FROM SPENT MUSHROOM COMPOST AND COAL TAILINGS



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For my family

Spent mushroom compost (SMC) is an agricultural waste disposed of in an unsustainable and environmentally degrading manner – mainly in landfills. For every 1 kg of mushrooms grown, approximately 5 kg of SMC is produced, where current generation in the UK is 200,000 t/a. Coal tailings, an industrial by-product from coal mining, are also discarded untenably in lagoons; removing these deposits will eliminate the associated environmental hazards. This project aimed to combine these waste materials into a suitable 'green' fuel for industry through thermal treatment, to produce energy from a sustainable source. Not only will this alleviate the issues regarding existing waste management strategies, but will also attempt to mitigate the environmental impacts of energy generation from non-renewable sources, such as anthropogenic climate change, through the generation of renewable energy.

This PhD research has shown that both materials had high moisture contents, which negatively impacted the calorific value (CV). Drying, though expensive, would thus be required prior to pelletisation and thermal treatment. Key pelletisation parameters were identified and manipulated to control product quality. Optimal values were experimentally-determined for pellet composition (50:50 wt% SMC:coal tailing ratio), moisture (10.5 %) and pressure (6000 psi/41 MPa); such pellets had a NCV of 16.11 MJ/kg. As these pellets were still friable, additional studies were carried out to further improve pellet quality, in terms of density, tensile strength and durability. Elevated temperatures and steam were considered, in addition to the use of starch and caustic soda binders, which were all successful to varying degrees.

Combustion, gasification and pyrolysis tests compared the raw SMC to SMC-coal tailing pellets, where pellet combustion performed better than the SMC alone, and fluidised-bed combustion was more efficient than the packed-bed. Although pyrolysis worked well, the CV of the fuel products were low, whereas gasification was unsuccessful. Consequently, in-depth studies into pellet combustion in a laboratory-scale fluidised-bed were performed, examining: (i) combustion/fluidisation air flowrates (4.9-10.7 kg/hr); (ii) fuel pellet feedrates (2.02-4.58 kg/hr); and (iii) sand bed depths (0.22-0.30 m). The impacts on temperatures, combustion efficiency and gas concentrations, including acid gas species were analysed. The most favourable operating conditions resulted in high temperatures for efficient energy recovery, with minimal pollutants, although the addition of secondary air jets could further improve the already high combustion efficiencies. While gaseous pollutants are unlikely to be an issue, as the emissions produced generally conformed to the Waste Incineration Directive, efficient particulate collection will be required to remove flyash from the gas stream prior to release to the atmosphere. Industrial implications were explored for heat and power generation, where mass and energy balances for a theoretical furnace, boiler and turbine set-up were completed for various fuel throughputs. Excess heat from the process could be utilized to dry the initial materials, but the economic analysis showed this would be costly – totalling ⅔ of overall pelletisation expenses. Assuming an overall process efficiency of 18.6 %, a steam turbine could generate over 10 MWe, based on an SMC-coal tailing pellet feedrate of 400,000 t/a – to simulate a large, centralised energy-from-waste facility. FLUENT, a mathematical model, was able to effectively replicate the results of the experimentation and was then used to model particle elutriation and entrainment to assess the suitability of the transport disengagement height provided.

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"Waste is a terrible thing to waste"

The X-Files, Season 3, Episode 12 – 'War of the Coprophages'

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NOMENCLATURE, NOTATION AND ACRONYMS

Latin Nomenclature:

A	m^2	Cross-sectional area of the bed
A_{cross}	m^2	Cross-sectional area of the reactor
b	-	Base of the ash sample during ash fusion tests
BR	kg/m^2hr	Burning rate
d	mm	Pellet diameter
d_p	μm	Mean bed particle size
D	g/cm^3 or kg/m^3	Density
f	dimensionless	Function of
g	m/s^2	Gravitational acceleration
G	-	Gasification of the SMC
h	m	Height of the bed above the distributor
h_f	°C	The fluid/flow stage of ash fusion
h_h	°C	Hemispherical stage of ash fusion
H_P	m	The maximum height of the pellet pile
H_o	m	The initial height of the bed
L	mm	Pellet length
m	kg	Mass of particles
m_{air}	kg/m^2hr	Air mass flowrate
M	-	Energy absorber
M_o	kg	The initial bed weight
$P_{no.}$	dimensionless	The number of pellets in a pile
Q	GJ/kg	Higher heating value of the fuel
Q_m	dimensionless	The amount of material in the pelletiser
U	m/s	Fluidising velocity
U_{mf}	m/s	Minimum fluidisation velocity
U_t	m/s	Terminal velocity
V_{mf}	m^3/s	Volumetric flowrate at the initiation of fluidisation
W_P	kg	Mean pellet weight
W_{max}	kg	The maximum weight the pellets can withstand
x	m	Coordinate
x_*	m	Moving coordinate
Y^a_f	dimensionless	Mass fraction of ash in the fuel
$Y^a_{K_2O}$	dimensionless	Mass fractions of the K_2O present in the ash
$Y^a_{Na_2O}$	dimensionless	Mass fractions of the Na_2O present in the ash

Greek Nomenclature:

ΔH	MJ/kg mole	Enthalpy of a reaction
ΔM	kg	Mass loss of the bed
ΔP	N/m^2	Pressure drop
Δt	hrs	The length of the ignition propagation or char combustion stage
ε	dimensionless	Void space in the bed
η_{CE}	%	Combustion efficiency, based on gas concentrations
μ	kg/m s or Ns/m^2	Viscosity of the fluid
ρ_b	kg/m^3	Density of the bed
ρ_f	kg/m^3	Density of the fluidising gas/liquid in the fluidised bed
ρ_o	kg/m^3	The initial bulk density of the bed
ρ_p	kg/m^3	Density of the particles in the fluidised bed
ρ_{pellet}	kg/m^3	Pellet bulk density
φ	dimensionless	Particle sphericity

Subscripts:

c	-	The char oxidation (combustion/gasification) stage
C	-	Coarse particles (with reference to the TDH)
F	-	Fine particles (with reference to the TDH)
i	-	The ignition propagation stage
sto	-	Stoichiometric air, where $\lambda = 1$

Abbreviations and Acronyms:

AI	Alkali index
ANOVA	Analysis of variance
ar	As received
ASTM	American Society for Testing and Materials
ATP	Adenosine triphosphate
BFB	Bubbling fluidised bed
BR	Burning rate
Cb	Cardboard
CFB	Circulating fluidised bed
CFCs	Chlorofluorocarbons
CHP	Combined heat and power
CS	Compressive strength
CV	Calorific value – described in Chapter 2.2.3
CWS	Coal-water slurry
daf	Dry-ash free
DM	Dry matter
EfW	Energy-from-waste
ESPs	Electrostatic precipitators
FGD	Flue gas desulphurisation
GCV	Gross calorific value
GWP	Global warming potential
HEP	Hydroelectric power
HFCs	Hydrofluorocarbons
HHV	Higher heating value
ICP-MS	Inductively-coupled plasma mass spectrometry
IFS	Ignition front speed
IR	Ignition rate
LFG	Landfill gas
LHV	Lower heating value
Mp	Miscanthus pellets
MSW	Municipal solid waste
NADP	Nicotinamide adenine dinucleotide phosphate
NCV	Net calorific value
NOx	Oxides of nitrogen
PAHs	Polycyclic aromatic hydrocarbons
Pc	Pine cubes
PCB	Polychlorinated biphenyls
PCDD/F	Polychlorinated dibenzodioxins and polychlorinated dibenzofurans
PCP	Pentachlorophenol
PFA	Pulverised fuel ash
PFB	Pressurised fluidised bed
PV	Photovoltaics
RDF	Refuse-derived fuel
ROC	Renewables Obligation Certificate
RT	Room temperature (usually around 20 °C)
SCR	Selective catalytic reduction

SMC	Spent mushroom compost
SMCA	Spent mushroom compost ash
SNCR	Selective non-catalytic reduction
SNRB	SOx-NOx-ROX-BOX
SOx	Oxides of sulphur
Sp	Switchgrass pellets
Sr	Switchgrass, raw
SRF	Solid recovery fuel
TCDD	2,3,7,8-tetrachlorodibenzo[p]dioxin
TCDF	2,3,7,8-tetrachlorodibenzofuran
TDH	Transport disengagement height
TS	Tensile strength
UHCs	Unburned hydrocarbons
UV	Ultra-violet
VOCs	Volatile organic compounds
WID	Waste Incineration Directive
Ww	Willow wood
XRD	X-ray diffraction

1

INTRODUCTION

Energy: it is the basis of all life on Earth and is vital for our existence, whether in terms of the sun's heat or electrical power. As the world becomes increasingly developed and the population expands, the need for energy grows; this should not be problematic as sufficient resources are available but the predicament is that energy consumption is growing at an ever-increasing rate and due to the sources used, it is becoming progressively less sustainable. Our dependence on non-renewable resources, primarily fossil and nuclear fuels, has a variety of associated environmental issues, first and foremost the pollution of the atmosphere – resulting in ozone depletion, acid rain and photochemical smog, as well as the anthropogenically-enhanced greenhouse effect leading to climate change. This, however, is not seen as the main cause for concern; the fact that fossil fuels are slowly running out is unfortunately considered to be a higher priority than the environment and much work has therefore been concerned with enhancing the use of the resources left through improving power station efficiencies.

Emissions reduction has also been a topic of focus, so the environmental impacts of energy generation are less significant. Although technologies are improving, it is clear they are not tackling the cause of this extensive problem, merely dealing with its effects. To manage the ensuing crisis at hand, further research into the availability and use of renewable energy resources, such as biomass, is desperately required, to develop appropriate technologies and meet future energy needs. As the issues with current energy production strategies increase, renewables look set for a progressively important role in the future. It is therefore necessary to investigate a wide variety of possibilities for these to be an unambiguous way out of the impending energy dilemma.

This chapter overviews different energy sources, focusing on renewables, mainly biomass. Energy production and the various environmental implications are also evaluated. Lastly, a background to the project is given and the aims and objectives are outlined.

1.1 OVERVIEW OF ENERGY RESOURCES

Energy sources can be divided into two distinct categories. The first of these is non-renewable resources – namely fossil fuels derived from the remains of animals and plants, which have been subjected to extreme temperature and/or pressure for prolonged periods and have been converted to substances we use as fuels, such as coal. Nuclear fuels also fall into this category. Secondly are the renewable energy options, which are by far the most diverse, comprising biomass, for example wood and forestry or agricultural residues, such as spent mushroom compost, the focus of this research, as well as a number of other technologies and natural resources.

1.1.1 Non-Renewable Energy Sources

Non-renewable resources are classified as those which are not replenished at the same rate they are used. Such energy sources are therefore fossil fuels and include solid (coal), liquid (oil) and gaseous (natural gas) forms. These substances were once organic matter but have been altered by a series of biological, physical and chemical processes. These are widely used as fuels today but take millions of years to develop and due to this, they are effectively not replaced and thus finite. As the use of these is intensive and their replacement extremely slow, the reserves available are rapidly decreasing; their use has been prolonged and they are now running out to the point where the predictions being made for how many years supply is left are somewhat alarming. Coal is used in power stations all over the world to generate electricity and the reserves, whilst still large, used to be enormous, though not all are easily obtainable. As the recoverable coal begins to run out, however, reserves that are at present uneconomical to mine will become more viable. Oil is widely-used, with many applications and the well-developed technologies have resulted in its rapid depletion. As conventional supplies have started to become exhausted and their costs have risen, unconventional sources, such as shale oil and tar sands, have become more viable and are now being used. The environmental implications are often more severe and extraction costs are also greater due to additional processing and refining. Natural gas is the most ideal fossil fuel, as it requires little processing, is more economic and produces lower emissions in comparison with coal and oil. Emissions, however, are still produced and there are issues with storing and distributing gaseous fuels.

The problems associated with the excessive use of these fuels have been well documented. The mining and extraction phases of coal, for example, have considerable risks, not only to the environment, but also to the people who are employed there; illnesses related to working in dusty, often carcinogenic, environments are unfortunately common. Furthermore, a variety of detrimental pollutants are released upon combustion, which leads to diverse environmental concerns, including the anthropogenically-enhanced greenhouse effect leading to global warming and large-scale climatic change, as well as the

issues listed above. The exhaustion of these fuels, coupled with the widespread environmental implications means their use is evidently unsustainable. Energy production and fuel resources in the future must therefore be environmentally-friendly and in continuous supply.

As a result of the numerous issues related to the use of fossil fuels, more sustainable energy sources have been developed. The use of uranium- and deuterium-based nuclear power has grown over the last few decades and their supply is thought to be practically infinite. This, in effect, solves the problem of our energy supply running out. There are however major environmental concerns. These begin at the start of the fuel cycle, with the mining of uranium-235; there are the dangers associated with mining in general, as identified above, as well as the risks due to the exposure to radioactive dust. Milling and grinding produce 'yellowcake' (U_3O_8), which contaminates the surrounding area if the radioactive tailings leach. At the enrichment plant, fuel fabrication and reprocessing have further environmental implications, as there is a risk of radioactive effluents in the waste (Dostrovsky, 1988). Disposal of spent fuel is equally environmentally degrading and one of the central controversies of this fuel, considering that there is much debate over what constitutes safe deposition sites. Decommissioning is also problematic. Nuclear accidents, such as those at Chernobyl and Three Mile Island, have done nothing to improve public opinion; both were caused by a combination of human error and design faults and continue to affect the surrounding areas and the health of those who survived. There are also issues relating to safety and consequently, its implementation is often controversial due to lack of public acceptance.

1.1.2 Renewable Energy Options

Renewables are natural sources of energy available for use that can be replenished or replaced at a comparable rate to which they are used (Sørensen, 1979). As the non-renewable resources above have many issues associated with their use, renewable energy is seen as an environmentally-practical and now an economically-viable option, thus the use of these sources is steadily increasing. Due to this, biomass and other renewables must now play an increasingly significant part in power generation and are therefore eventually and inevitably set to become the energy resources for the future. There are many key advantages over the previous energy sources. Importantly, renewable energy options are able to be used continuously as they are either inexhaustible or they are replenished, and additionally, their environmental implications are significantly less. The development and utilisation of renewable energy sources therefore seems to be a certainty, as well as a necessity, for the future of power generation.

1.1.2.1 Introducing Biomass as a Renewable Energy Resource

Biomass is the organic material from plants that live or once lived within the earth's biosphere. This biomass, along with its associated organic wastes, is a great energy resource that is continuously replaced (Ramage and Scurlock, 1996; McKendry, 2002a). Biomass, for use as a fuel to produce heat and power, has to be the resource with the longest history of use and this solar-derived energy source has been vitally important for societal development across the globe for thousands of years.

Flora are able to store solar energy, which is subsequently used for power, through photosynthetic processes, converting carbon dioxide (CO_2) and water (H_2O) into oxygen (O_2) and a carbohydrate ($C_6H_{12}O_6$), via a light-induced reaction. The overall equation for this is:

$$CO_2 + H_2O \longrightarrow {}^1/_6\, C_6H_{12}O_6 + O_2 \qquad (1.1)$$

The net energy required, added by solar radiation, to form $C_6H_{12}O_6$ via the above reaction, is 4.66×10^{-18} J (Sørensen, 1979). This process occurs in two distinct phases. The first stage is the photodissociation of water, as the chlorophyll, the green pigment found in plants, absorbs light:

$$2H_2O \xrightarrow{\text{light energy}} O_2 + 4H^+ + 4e^- \qquad (1.2)$$

The energy is then carried by cations and electrons until the nicotinamide adenine dinucleotide phosphate (NADP) compound becomes $NADPH_2$, and adenosine triphosphate (ATP) is formed. In the second stage, known as the Calvin cycle, a high energy reaction takes place in the dark, where these molecules produce the carbohydrate (Ramage and Scurlock, 1996):

$$4H^+ + 2CO_2 \xrightarrow{ATP} 2[CH_2O] \qquad (1.3)$$

This process, however, is not efficient in terms of converting all available sunlight to energy; in fact, it is normally less than 1 % (McKendry, 2002a). It is this stored chemical energy that is extracted when the biomass is used as a fuel resource.

There are many advantages to energy production from biomass. A range of different types can be used, thus some form can be cultivated almost anywhere and there is also essentially an endless supply. Its versatility is highly beneficial: not only can it be combusted, but it can also be processed to produce fuels with greater calorific value (CV), that can be utilised for a range of purposes, from commercial power production to the transport industry. Combustion of fossil fuels, essentially fossilised biomass, releases CO_2 that has not been present in the atmosphere for thousands, even millions, of years, which increases the amount present and therefore directly contributes to global warming (McKendry, 2002a). Burning biomass, however, has no net CO_2 emissions (CO_2-neutral) since it has recently been absorbed and will be reabsorbed during the photosynthetic growth of new biomass: the carbon cycle at work, albeit anthropogenically-modified. There is unfortunately often a considerable time-lag between the release and uptake of CO_2 during biomass re-growth and it may therefore be necessary to provide mitigation strategies to deal with the consequences (McKendry, 2002a). In addition to aiding the alleviation of the greenhouse effect, there are a number of other environmental benefits, including reducing regional pollution, conserving water and soil, and integrating the agricultural and energy sectors (UNEP, 1991).

1.1.2.2 Other Renewable Resources

Besides biomass, there are a wide variety of other renewable resources. As with all renewable energy, pollutants are not as profuse, making them environmentally-friendly on this level. The driving influences,

which control the nature, direction and amount of progress made in this field, are the market forces and the political decisions – not only the legislation concerning environmental, energy and climate policy, but also industrial subsidies (Kamp, *et al.*, 2004; Şahin, 2004; Brandt and Svendsen, 2006). Public opposition, as with nuclear power, is another dominating influence; there is often resistance to the adoption of renewable energy due to the other environmental implications. What it is important to realise is that whilst there will be environmental effects to some extent regardless of which energy source is adopted, renewable resources tend to have much fewer impacts than non-renewables; the effects are also usually more localised. Some options are prominent, such as the use of wind and hydroelectric power (HEP), while others are not so well publicised in the UK but have been used to great effect elsewhere, such as geothermal. Others are currently being developed, such as hydrogen, fuel cells and some water-based technologies. Developments and advances are being made continuously to improve these.

Solar energy technologies are varied and consist of two types – solar thermal and photovoltaics (PV). Solar thermal technologies (passive and active designs) use solar energy – heat from the sun – to heat a building or a substance, usually water, and is often fully integrated into its design (Everett, 1996). Solar thermal power generation is also used in this way, for instance using parabolic troughs or dishes. PV is based on the differential electrical conductivity between semiconductor materials, used primarily in grid-connected or stand-alone systems. Although solar panels, which convert radiation directly to electricity, can be expensive, PV is both an attractive and straightforward form of energy generation and is already economically viable for certain remote locations (Jäger-Waldau and Ossenbrink, 2004). There are issues concerning the consistency of the radiation supply and thus where PV cells can be applied, although the conversion efficiency is extremely high (Boyle, 1996).

More than 4000 years ago, wind was used as a source of power, harnessed by windmills, and subsequent technological developments have enabled wind to now be a significant and widely-used renewable energy resource, becoming more convenient and increasingly economically-viable (Taylor, 1996). It is the fastest growing renewable source, with annual growth rates of 20-30 % (Jäger-Waldau and Ossenbrink, 2004). An important benefit is that resources are fairly evenly distributed, although its unpredictability, the visual intrusion and efficiency (restricted to 59.3 % by the Betz limit) can be challenging (Taylor, 1996). Nevertheless, this efficiency is still notably higher than many other energy production methods.

Many water-based technologies are used to harness energy, comprising HEP – the use of water flowing in rivers – as well as four ocean systems: waves, tidal, currents and thermal gradients. HEP is an indirect use of solar power as water evaporates when heated by the sun, where condensation and precipitation close the water cycle. Placing dams and turbines across rivers enables stored potential energy to be captured often at high efficiencies and is an already well-established practice (Ramage, 1996; Ristinen and Kraushaar, 1999). Although there are limitations to covering land with a reservoir, like disrupting the ecological balance and dam failures, small-scale schemes minimise these impacts (Roberts, *et al.*, 1990).

Energy extraction from waves, the first ocean energy system, can be exploited through a variety of methods, as devices can be placed on or offshore and can float or be fixed to the sea-bed. There appear to be few environmental impacts from most schemes (Duckers, 1996). The continuous gravitational interactions between the earth and the moon mean tidal bulges can be used twice a day throughout the year to produce energy; a barrage can be constructed across an estuary to trap water at high-tide to be released at low tide and produce a surge of power. Unlike wave power, tidal schemes are often large, require vast financial inputs as well as long construction periods, and can have complex ecological impacts (Roberts, *et al.*, 1990). The final two ocean energy systems, currents and thermal gradients could be utilised for power generation, as the oceans absorb solar radiation (Ristinen and Kraushaar, 1999). Although there are advantages, for example the sub-aqua turbines are located far out to sea thus limiting the impacts on coastal populations, the conversion efficiency is low. These technologies are also in a fairly embryonic state.

Although the interior heat of the earth is fairly constant, in some locations, such as those which have hot springs or experience volcanic activity, the heat flux to the surface is much greater and can be used for geothermal energy production. There are two distinct types: 'hot dry rocks' and hydrothermal resources (subcategorised as hyperthermal and low-conductivity strata). The first is where heat stored within impermeable rocks is extracted by pumping water into man-made fractures. While only a few sites are available and schemes are often expensive, where it is used, it provides large proportions of regional energy, which are made more economic by improving the efficiency using combined heat-and-power (CHP), as in Southampton (Southampton City Council, n.d.).

Fuel cells facilitate the conversion of a fuel's chemical energy to electrical power without combustion, with a higher degree of efficiency than a conventional engine (Everett and Boyle, 1996; Boudghene Stambouli and Traversa, 2002). Moreover, they have a high energy density and an array of applications, including power generation and transportation (Srinivasan, 1999). Another distinct advantage is that there are a range of types, depending on the fuel used, which includes biomass (Ramage and Scurlock, 1996). Hydrogen is another renewable energy source, as it is a medium for storing energy, particularly in fuel cells (Boyle, 1996). It can be produced by conventional or renewable fuels, by the electrolysis of water or by PV cells and is a 'premium-quality energy carrier'. There are a number of technological barriers to overcome and as it is only just emerging, it is thus still extremely expensive (Ogden, 1999).

1.2 ENERGY PRODUCTION AND ENVIRONMENTAL ISSUES

As can be seen from the above discussion of energy, it is vital for our existence and there is an increasing demand for it. Its sources, however, are cause for concern, particularly due to their environmental implications. The detrimental impacts of using fossil fuels are concerned primarily with the emissions from combustion. Although abatement and removal techniques are employed to reduce pollutant levels before flue gases are released, these technologies are relatively new and anthropogenic emissions have

been building up in the atmosphere for some time. Some compounds, such as carbon dioxide, are still released in vast quantities. The varieties of elements that make up fuels like coal mean a number of pollutants are emitted, which have varied environmental effects.

1.2.1 Greenhouse Gases and the Greenhouse Effect

The greenhouse effect is the natural phenomenon of atmospheric heating caused by compounds in the air referred to as 'greenhouse gases'; these, which are detailed in Table 1.1, trap heat making it warm enough for our planet to be inhabitable. The mechanism for this is expressed in Figure 1.1.

GREENHOUSE GAS	CONCENTRATION IN ATMOSPHERE		GLOBAL WARMING POTENTIAL (GWP)
	PRE-INDUSTRIAL	1998	
CO_2	280 ppm	370 ppm	1*
CH_4	750 ppb	1750 ppb	23
N_2O	270 ppb	314 ppb	296
CF_4	40 ppt	80 ppt	5700
CFCs	0	4-533 ppt	4600-14000
HFCs	0	0.5-14 ppt	120-12000
SF_6	0	4.2 ppt	22200

Table 1.1: Table showing the changes in the atmospheric concentration of selected greenhouse gases. Sources: IPCC (2001); National Oceanic and Atmospheric Administration (2004)
* The GWP of CO_2 is 1 as this is the reference gas, to which other GWP are related.

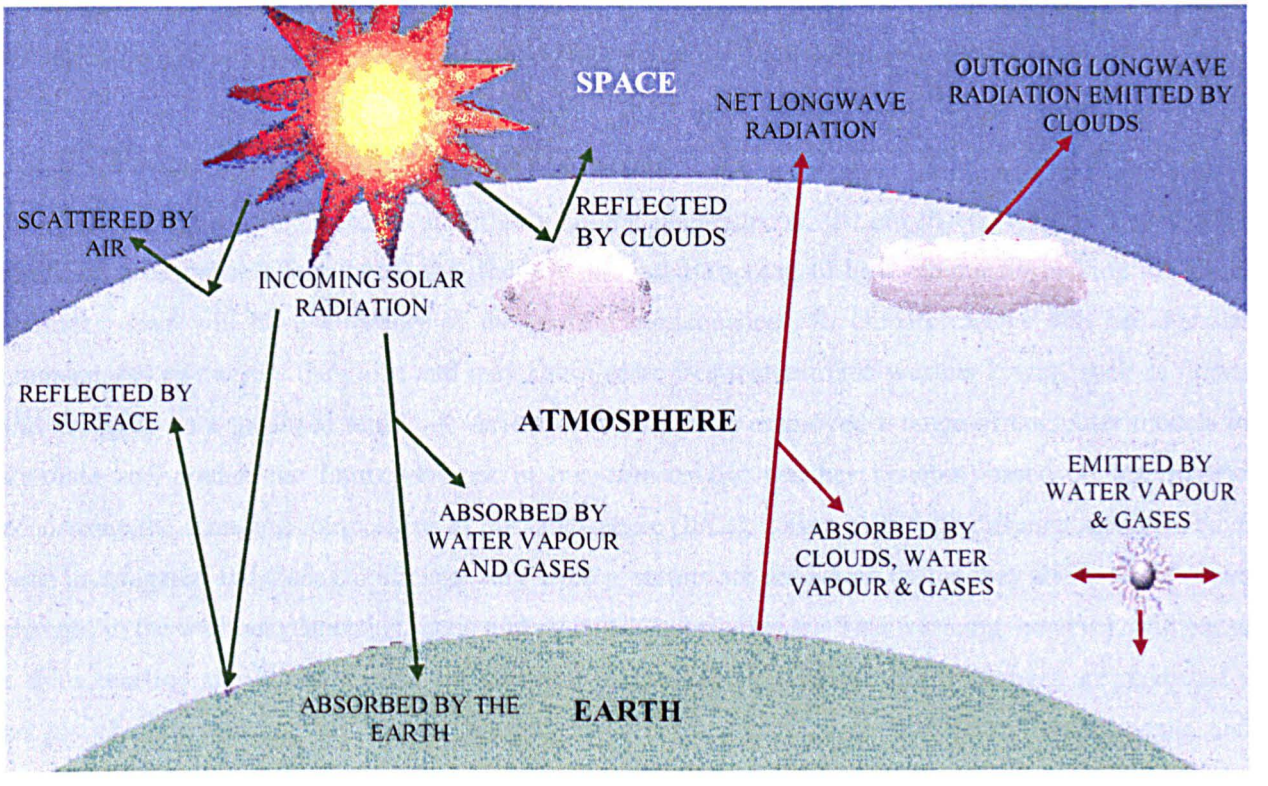


Figure 1.1: The natural (green) and the anthropogenically-enhanced (red) greenhouse effect. Source: NERC (2001)

The concerns over this are that increasing amounts of these gases are present in the atmosphere due mainly to fossil fuel combustion, essentially because of energy production and transport, although there

are other sources. It is now thought that significantly increasing the atmospheric concentrations of such gases will increase the amount of heat that is trapped – the anthropogenically-modified or enhanced greenhouse effect, also shown in Figure 1.1. As seen from Table 1.1, the concentration of various species, such as CO_2 from combustion and methane (CH_4) from biological decomposition and natural gas leakage, has dramatically increased. Many complex compounds, namely CFCs (chlorofluorocarbons), HFCs (hydrofluorocarbons) and SF_6 (sulphur hexafluoride) from refrigeration, aerosols and the semi-conductor industry respectively, are not naturally present in the atmosphere. The concentration of tetrafluoromethane (CF_4) has also increased noticeably, more than doubling since the eighteenth century. Perhaps more importantly, as Alexander (1996) states, these more complex substances have higher global warming potentials (GWP), which has been defined by the IPCC (2001) as:

> An index, describing the radiative characteristics of well mixed greenhouse gases, that represents the combined effect of the differing times these gases remain in the atmosphere and their relative effectiveness in absorbing outgoing infrared radiation. This index approximates the time-integrated warming effect of a unit mass of a given greenhouse gas in today's atmosphere, relative to that of carbon dioxide.

This means that although some of these compounds are only found in extremely low concentrations, for instance certain HFCs, the impacts they have on the climatic system are vast, relative to that of CO_2. There are also other species related to this phenomenon that are not included in the table. Atmospheric water vapour, for example, also contributes to the natural greenhouse effect, although due to the closed nature of the hydrological cycle, the amount is static and not anthropogenically altered.

1.2.2 Climate Change and Global Warming

Although the greenhouse effect is an entirely natural phenomenon, the enhanced or anthropogenically-modified greenhouse effect means that there is increased trapping of heat, ultimately making the Earth warmer. This will have a variety of devastating consequences, as climate change will see average temperatures rise across the globe and may cause more frequent extreme weather events, such as floods and droughts on a localised scale. A variety of studies have employed a range of computer models to simulate and predict the future changes in our climate and weather systems, based on information concerning the changing composition of our atmosphere (IPCC, 2000). Although different scenarios have been investigated and these simulations vary widely, results are consistent in that they all show definitive changes in the way our planets' climatic and related systems operate. This warming, however, will cause a chain reaction altering more than just the temperatures we experience. Many changes are predicted – not just climatic warming but changes in weather patterns in general, such as extreme weather events, and over time, an ultimate change in climate coupled with rising sea-levels. This will lead to a shift in the distribution of major world biomes, particularly the expansion of deserts (desertification) and in turn, will have an enormous effect on the inhabitants of these places, both people and animals. The sea-levels will rise due to thermal expansion of the sea and also due to the melting of ice caps and glaciers, flooding many low-lying areas, the worst affected being poorer countries, such as Bangladesh. Other implications

of our actions include alterations of ocean thermal currents, the biological impacts of disease or world pandemics, and even the extinction of some species. The financial repercussion of dealing with such a multitude of global impacts will obviously be extreme.

1.2.3 Other Environmental Problems

In addition to the warming of the climate and its subsequent effects on the weather systems and hydrological cycle, there are a number of other environmental issues caused, at least in part, by the combustion of fossil fuels. These include acid rain, photochemical smog and ozone depletion. Acid rain is caused by various pollutants found in the flue gases released from power stations, although there are other sources (Alexander, 1996). These include oxides of sulphur and nitrogen (SOx and NOx), as well as other acid gases, such as hydrogen chloride (HCl). This is referred to as 'wet' acid rain as these species dissolve in the water of precipitation or clouds. 'Dry' acid rain occurs when these acid gases are adsorbed onto the surface of dust particles, which then also fall to Earth and are deposited. Although these formation routes sound simple in theory, in practise, the causes are often more complex, due to the multitude of processes occurring in the atmosphere. These acids have a variety of consequences; the acidification of lakes has caused widespread problems throughout Scandinavia, for example killing fish, and many areas of German forests have experienced defoliation and subsequent deforestation, as the trees can no longer survive in such acidic conditions. Buildings, particularly those built from limestone, are also vulnerable and it is not uncommon to find extreme amounts of weathering and erosion due to this on historic buildings. The obvious solution is to reduce the emissions of these substances through various removal strategies, although more stringent legislation is required to control emissions to a higher degree.

There are two types of smog: the first is sulphur-based, caused by the release of SOx, known as 'acid mist', and the second is photochemical (Figure 1.2), caused by various emissions from power stations, including NOx and unburned hydrocarbons (UHCs). These species react in the presence of ultra-violet (UV) light, in what is known as the nitrogen photolytic cycle, and can result in severe health problems.

Figure 1.2: Photograph of photochemical smog in Los Angeles, USA.
Source: Su (2002)

The stratospheric ozone layer is 15-35 km above the surface of the earth, which filters out much of the harmful UV radiation to protect us. Many compounds released from power generators react with ozone

(O_3) to deplete it, such as NOx and CFCs, which undergo reactions to convert O_3 to O_2. The UV radiation found at these altitudes also facilitates the depletion of O_3 by the photodissociation of O_2 to form radicals and initiate the reaction. The combustion of fuel in power stations may have a limited affect, but the emissions released at high altitudes, specifically from aircraft, are the cause for most concern.

1.2.4 Non-Renewable Vs. Renewable Energy: The Rise of the Renewables?

As previously discussed, all energy sources have their limitations. The environmental issues are of primary concern as they can and do have direct influences on our lives, now and in the future. Moreover, it can be seen that the environmental effects of non-renewable sources are far more widespread than those of renewables. This surely suggests that we should be making more use of the opportunities we have to utilise and research further the renewable resources available. The environmental damage resulting from the use of fossil fuels include increasing amounts of CO_2 and other greenhouse gases in the atmosphere, leading to an enhanced greenhouse effect and climate change on a global scale, as well as more localised impacts, like photochemical smog and acid rain. As these issues are generally not applicable when considering renewable sources, the environmental problems are considerably less. These environmental difficulties and other issues associated with the use of non-renewable fuels must mean that the future of energy generation will change dramatically. There are many factors driving change in the energy sector, such as the increasingly stringent legalisation, market forces and public opinion. These pressures on present energy procedures represent challenges that essentially cannot be overcome. This has lead to there being more reasons to adopt renewable technologies for power production, coupled with fewer to continue using non-renewable sources. In addition to these well-publicised concerns, fossil fuel reserves will eventually be exhausted, leading to a considerable energy shortage if alternative supplies are not found. Due to this, energy production in the future will have to be cleaner and more efficient. Biomass, such as spent mushroom compost and other renewables therefore seem like the green option for power generation. Whilst there are some environmental impacts from these, their adoption will considerably reduce our current negative influences, although not necessarily reverse the effects we have already had.

In recent years, investigations into these areas have come to the forefront of research in the energy sector. Whilst some focussed on improving efficiency and making energy production from fossil fuels more environmentally-sound, the majority looks at various renewable options and their potential. Due to this, the employment of these sources has become increasingly rapid of late. McKendry (2002a) discusses factors which have brought about a restored interest in the use of biomass and derived biofuels; one of the most important is the contribution of other sources, namely fossil fuels, to greenhouse gases. Given that biomass and other renewables are CO_2-neutral, it has now re-emerged as a significant energy source.

1.3 BACKGROUND: SPENT MUSHROOM COMPOST AS A FUEL

As the mushroom growing industry continues to develop, spent mushroom compost, hereinafter SMC, production is therefore also increasing. At present, its generation rate is about 200,000 t/a in the UK.

Disposal is often problematic due to the large quantities produced, particularly as it is disposed of in landfill sites or is spread as a fertiliser on agricultural land; both are unsustainable and environmentally degrading, and consequently disposal is the most significant barrier to future developments in this industry. In order to remove this major obstacle to allow expansion and security, an alternative disposal route is needed, whereby SMC can be put to use in a sustainable and environmentally-friendly manner. Although a number of studies have investigated a variety of possible uses for SMC, mainly agricultural and industrial applications, few have considered its use as a potential energy feedstock. Williams, *et al.* (2001a), Williams (2001) and McCahey, *et al.* (2003) report no previous 'combustion trials' have been carried out on SMC and thus little other literature is available regarding this. Although the properties of SMC were evaluated and compositional analyses were performed in these studies, as will be the case here, they did not explore SMC pelletisation, or its combination with a coal tailing binder.

Using SMC combined with higher CV coal tailings to act as a binder and a secondary fuel, pellets can be made and have the potential to provide heat and/or power in a variety of industrial situations. In the UK, as only a small percentage of energy comes from renewable resources, it is important to increase this, not only to meet energy legislation requirements, but also to minimise or at least lessen our environmental impacts. Additionally, the amount of energy produced from unsustainable fuel resources could be reduced, consequently lowering the greenhouse gases that are emitted, and mitigating at least in part, the impacts of global warming and climate change, as well as other the environmental issues previously described. The use of these materials will eliminate the need for their undesirable disposal and will also be beneficial in aiding the cleaning and reclamation of contaminated land. The primary purpose, therefore, of using SMC and coal tailings as energy sources is to increase the amount of renewable power generated, and thus attempt to mitigate impacts of anthropogenic environmental problems. Through this, it is possible to make use of wastes, reduce the amount of SMC going to landfill and aid the clean-up of contaminated areas. The key purposes of pelletisation are to improve fuel properties, such as energy density, and to enable cheaper and easier transportation, storage and handling.

1.4 SYNOPSIS OF THE RESEARCH

The rationale for this research was to complete an investigation concerning the use of SMC and coal tailings as renewable fuels, through combining a comprehensive review of literature and theory, with extensive experimental procedures relating to the manufacture and use of SMC-coal tailing pellets. The key themes and ideas within this field were explored in-depth, to define the research area and clearly outline the gap within it. Experimental procedures were outlined, based on the appraised literature and theory, to evaluate the composition and properties of both materials, and subsequently explore the practicalities of forming fuel pellets from these substances. Additional information concerning their pelletisation was sought, through an assessment of specific variables, which were manipulated and their effect quantified, to define the optimum pelletisation conditions. Combustion, pyrolysis and gasification were compared, then further experimental procedures considered the efficiency, energy recovery and

emissions from fluidised-bed combustion, examining the impact of different air flowrates, pellet feedrates and sand bed depth. Complementary theoretical and mathematical modelling were also completed.

1.5 AIMS AND OBJECTIVES

The purpose of this research was to discover the potential for reusing SMC and coal tailings as fuels through physical processing to form pellets. This work was divided into sections – a comprehensive literature review, research into the theoretical background, extensive experimental work and an examination of industrial applications; the aims and objectives of this study therefore are as follows:

1. **To complete a broad literature search concerning -**
   - biomass as a source of energy and its related legislation,
   - the two waste materials utilised for this PhD research – SMC and coal tailings.

2. **To investigate thoroughly various theoretical topics relating to -**
   - thermal treatments for energy production and their associated clean-up systems,
   - fluidisation and fluidised-bed combustion,
   - pelletisation.

3. **To outline and execute experimental methodologies for the analysis of -**
   - the material characteristics of SMC and coal tailings,
   - the pelletisation of the waste materials,
   - preliminary comparisons and advanced thermal treatment tests for SMC and coal tailings.

4. **To examine the industrial applications and implications of these fuels with regard to -**
   - FLUENT modelling concerning thermal treatment technologies,
   - heat and power generation,
   - meeting legislation,
   - the costs of processing and using these fuels.

1.6 OUTLINE OF THESIS

This thesis consists of twelve chapters. Chapter 1 established the background to this research area. Chapter 2 contains an overview of biomass fuels and relevant legislation, as well as exploring the generation, properties and potential uses of SMC and coal tailings. Chapter 3 presents a review of thermal treatment technologies, as well as the formation and removal of pollutants produced from these. Chapters 4 and 5 outline the theory of fluidisation, concerning fluidised-bed combustion and the theoretical background to pelletisation. Chapters 6 through 9 outline the methodologies, results and analyses of the material characterisation, pelletisation, the comparison of thermal treatments and the in-depth investigation of fluidised-bed combustion. Chapter 10 considers the industrial impacts of the use of such fuel pellets, focussing on FLUENT modelling and heat/power generation. Chapter 11 contains a broad discussion, culminating in a consideration of the wider industrial applications and lastly, Chapter 12 outlines the conclusions and future work to complete this thesis.

2

LITERATURE REVIEW

2.1 INTRODUCTION

This literature review thoroughly investigates key topics relating to this work, including: the types of biomass used as energy sources, legislation governing energy generation and waste management, and the materials utilised as energy resources here – SMC and coal tailings. Biomass is a renewable energy source, a solar energy store that can be exploited in a sustainable manner and replenished whilst previous stocks are used. There are many environmental advantages of using renewable energy compared to conventional fuels; there are reduced greenhouse and acid gas emissions and it can provide fuels for heating, power generation and transport, as well as chemicals for industry (Easterly and Burnham, 1996). Biomass therefore is an imperative way to move past our fossil fuel-dependency for all currently reliant sectors. Biomass sources can be organised into various groups, however, there are a number of these classifications (see Easterly and Burnham, 1996; McKendry, 2002a). The subcategories within the two main groups (i) waste and by-products and (ii) energy crops are explored here, with respect to their availability and use. The properties and composition of various biomass fuels are compared, along with the economic and environmental aspects of biofuel production. The concepts and key policies concerning waste and energy legislation are also outlined.

SMC is the waste from the cultivation of edible mushrooms, composed of a surface casing layer and a substrate underneath (Williams, *et al.*, 2001a). It is a significant by-product of the now commercial and large-scale mushroom-growing industry. The themes considered are: the formation of the compost; its constituents and properties; and its production rate. SMC utilisation has been investigated for a number of purposes, which is important as it creates excellent opportunities to divert it from landfill.

Coal is a fossil fuel, although its formation is distinctly different from oil and natural gas. It is a naturally-formed, complex hydrocarbon, in essence a sedimentary rock, produced during changes to plant remains over time (Speight, 1994; 2005). Since the industrial revolution, it has been commercially combusted in power stations for generating heat and power. When it is mined, many parts do not meet the quality criteria and these substances, coal fines, are mixed with water, forming slurry or tailings, which are disposed of in lagoons (Radloff, *et al.*, 2004; Speight, 2005). The formation, development and composition of coal has been examined briefly and the resultant coal tailings lagoons also discussed. The quality, quantity, composition, properties and uses of coal tailings have also been explored.

2.2 BIOMASS AS AN ENERGY SOURCE

2.2.1 Wastes and By-Products

Energy from waste and by-products falls into distinct categories, comprising commercial, industrial and municipal sources (McGowin and Wiltsee, 1996). Within these categories, there are many types, including agricultural and forestry residues, municipal solid waste and sewage sludge. SMC and coal tailings are from agricultural and industrial sources, which are reviewed in detail in Section 2.4 and 2.5.

2.2.1.1 Agricultural Residues

Agricultural wastes can be further sub-divided depending on the nature of the activity. The first is crop wastes, both tropical and temperate, where the types of non-woody crops used include straw, bagasse, rice husks and coconut wastes among others, which make good quality fuels. The type obviously varies depending on the location of the farming activity. Straw waste, found in temperate climates, for instance, can no longer be burned in the field due to pollution problems, so it is used as a fuel, often in on-site power stations or in regional biomass energy generators (Easterly and Burnham, 1996; Ramage and Scurlock, 1996). These areas also produce vast amounts of other crop wastes, such as potatoes, beet tops and damaged fruit and vegetables, as well as large volumes of domestic and commercial garden wastes (Ramage and Scurlock, 1996). Crop residues from more tropical climes are also varied, for example sugar cane, rice husks and coconut waste, many of which are used directly at the processing plants as fuels, via combustion, although biological treatments and other thermal processes are also common to convert them to more useful products through enhancing their energy density (Ramage and Scurlock, 1996). There are many concerns regarding the use of crop residues, the main one being that there are a number of competing uses, including composting, fertilisers and animal fodder. Other drawbacks are the difficulties associated with storing, transporting and handling such bulky materials and the seasonality of their availability (Easterly and Burnham, 1996; Wereko-Brobby and Hagen, 1996).

Animal sewage and other waste from extensive or intensive animal husbandry can also be used and is the second category within agricultural residues (Wereko-Brobby and Hagen, 1996). Although this is not common in the UK, many countries, such as Denmark, make use of this due to their large animal farming

businesses. One option is to combust the waste directly and use the energy to produce heat and power. These wastes can also be utilised to produce biogas. Using a digester, continuous or batch digestion can occur where the heat from the bacterial action is normally sufficient to maintain an ideal temperature for this process (Ramage and Scurlock, 1996). The fuel produced can be used for heat generation and/or electricity production. Even if this does not produce vast amounts of fuel for commercial or even domestic use, it is beneficial and therefore this is often used simply as a method of waste disposal, since there are sometimes large quantities of manure available and only a small proportion is required for fertilisers (Ramage and Scurlock, 1996). Sewage sludge can also be treated in this way. Anaerobic digestion is discussed in more detail with reference to biomass processing in the following chapter.

The use of agricultural residues as a conventional fuel substitute has a number of issues, as described by Werther, *et al.* (2000); these problems cover a range of factors, specifically the material characteristics. The main ones considered within this detailed article by Werther, *et al.* (2000) are the high moisture content, low bulk density, high ash content (with the associated problems of corrosion, slagging, fouling and poor handling) and the detrimental emissions produced.

2.2.1.2 Forestry Residues

Wood residues come from several woodland and forestry sources: timber processing waste, logging residues, sawmills, urban tree trimmings and the pulp and paper industries. Although many of these are able to recycle wastes within their process, significant amounts are still produced, which can be used for energy generation. Forestry management also generates large quantities of residue when specific practices known as 'culls' are employed – where a number are located together, it can be economical to transport residues to a centralised power plant for sustainable energy production for the community (Easterly and Burnham, 1996). This can be done without exhausting the forest through replanting and regeneration. Other practices exist, such as thinning, trimming and removing dead trees, to provide further fuel (Börjesson, *et al.*, 1997). If the biomass is large enough, it can be chipped and directly combusted in specialised burners (Ramage and Scurlock, 1996). As is often the case, the bulk density is low, while the moisture content is high and this, coupled with the fact that forestry management locations are usually remote, means it is not economic to transport these wastes long distances (Ramage and Scurlock, 1996). Börjesson, *et al.* (1997) considered the issues relating to the use of forestry residues: these were primarily the environmental, economic and technical limitations, as well as the manufacturing conditions, area available and yields produced. In some circumstances, there is competition for these wastes, mainly with the construction industry; fertilisation, however, can maximise yields. Werther, *et al.* (2000) further discussed many of these issues.

2.2.1.3 Municipal Solid Waste and Sewage

The production of waste from domestic, commercial and industrial sectors is vast, where households in the UK alone produce in excess of 25m tonnes each year, and unfortunately the majority ends up in

landfill (Ramage and Scurlock, 1996). This municipal solid waste (MSW), the general composition of which is shown in Table 2.1, can be made use of to produce heat and power and is thought to be a main source of renewable energy (Easterly and Burnham, 1996). This includes its direct incineration, the use of landfill gas or the production of refuse-derived fuels (RDF) or solid recovery fuels (SRF). The use of MSW is often high on the environmental agenda, as waste is diverted from landfill, except in the case of landfill gas. Some waste is both combustible and recyclable, so the relative economics of these decide its fate. According to Eastop and Croft (1990), if just a small proportion of the waste in the UK was used as fuel, this would result in considerable reductions in fossil fuel consumption and decrease landfilling.

CONSTITUENT	% WEIGHT
Paper	45
Plastic	6
Ferrous Metal	5
Aluminium	1
Glass	9
Other Organics	31
Other Inorganics	3
Total Moisture	30
As-received Ash	25
Oven Dry Ash	36

Table 2.1: General composition and properties of unprocessed MSW.
Source: Easterly and Burnham (1996)

Direct combustion of MSW, without pre-processing or sorting, is the simplest and cheapest way of utilising this waste, specifically for energy recovery through CHP or just to generate electricity. The plant at Edmonton, London, operates at an efficiency of 13 % and although this is not high, this is a better use for this waste than landfilling (Eastop and Croft, 1990). There is also an energy-from-waste (EfW) facility for power generation in Sheffield, producing electricity and district heating for much of the city (Figure 2.1); this means 63 % of MSW generated here is used for energy recovery and only 16 % goes to landfill. The use of MSW incinerators was previously considered to be a waste disposal option, but now more emphasis is placed on energy recovery, in the form of providing heat and power to the surrounding populations. Obviously using MSW in this way is an alternative to disposal, but the problems concerning current energy generation methods can also be mitigated in this way.

Figure 2.1: Aerial view of the energy recovery facility in Sheffield.
Source: Onyx Sheffield, Ltd. (2006)

As the composition of MSW is not ideally-suited to combustion, processing or treating it is often useful to lower the moisture and increase the energy density (Ramage and Scurlock, 1996); this also makes it easier to transport, store and handle, significantly reducing these costs. These issues and the subsequent processing of MSW have lead to the development of RDF and SRF, that are utilised in conventional power stations, either by combusting them on their own, or co-firing them with coal. A variety of products are formed from separating, drying and densifying (pelletisation) the waste to improve its characteristics, thus enhancing its suitability for combustion (Ramage and Scurlock, 1996). Pellets can be formed to increase the bulk and energy densities of the waste as well as eliminating moisture; prior sorting of non-combustible material is usually also required.

Allowing the natural decay of MSW produces methane and carbon dioxide gases, but also produces odorous and toxic gases that are problematic and can lead to explosions. Due to this, landfill sites necessitate careful management. By placing MSW in highly regulated sites, decay is controlled and the gases produced can be tapped and used as fuel, preventing explosions and eliminating the need for passive venting. Landfill gas (LFG) tapping and energy recovery reduces the amount of fossil fuels required for energy production and limits the amount of environmentally-detrimental pollutants released from landfill. Due to difficulties with gas extraction and the management of conditions, generally less that 50 % of LFG is recoverable. Although combusting LFG, the main constituent of which is CH_4, means CO_2 is released, it is notably less harmful to the environment in terms of GWP than simply venting the CH_4 to the atmosphere (Ramage and Scurlock, 1996).

Biogas can be formed from sewage sludge, as stated above, and subsequently used for heat and power generation. This is usually done on a large scale, though countries such as China and India are making these available on a much smaller scale for use with municipal and animal sewage (Ramage and Scurlock, 1996). Another option, as with animal waste, is direct incineration, however, the moisture has to be lowered considerably to work effectively (Ramage and Scurlock, 1996).

2.2.1.4 Other Commercial and Industrial Wastes

There are also a number of other commercial and industrial wastes that can be used to provide energy. An example of this type of waste is the use of tyres. A large number are disposed of every year, but unfortunately a considerable proportion is not suitable for energy use, even though they have a substantial energy content; their CV is approximately 32 MJ/kg (Ramage and Scurlock, 1996; DTI, 2006). Some power plants do make use of this waste and can incinerate millions of tyres each year for energy recovery, particularly those which co-fire them with coal, although there are several issues associated with this (Stopek and Justice, 1993). There are also problems with utilising other types of waste material, especially if they contain chemicals that can be potentially hazardous. Their use needs to be carefully investigated before they are employed to ensure the safety of people and the environment. Certain clean-up technologies can be used to combat some of these problems.

2.2.2 Energy Crops

Biomass grown specifically as a means to produce energy are known as 'energy crops', although they are also often referred to as 'virgin biomass' (Jäger-Waldau and Ossenbrink, 2004). There are certain characteristics that are considered important for energy crops, including: high dry matter yield per hectare; low energy and nutrient inputs with high energy output; low costs; and few contaminants or potential pollutants (McKendry, 2002a). Many suggest that in order for biomass to make a significant contribution to power generation in the future, the use of energy crops will need to be extensive, as it could potentially be the largest biomass resource (Easterly and Burnham, 1996). Of these crops, there are many categories into which they can be divided; herein, woody crops, C4 and herbaceous crops, and biomass grown specifically for processing will be considered. Due to their variety, there are many potential uses for these commercially.

2.2.2.1 Wood

Wood must be the earliest used fuel, thus growing and using it as a fuel today can only be a logical progression from its use in the past. This is seen particularly in Asia, Africa and South America, where wood is a primary source of fuel for both domestic and industrial sectors (Ramage and Scurlock, 1996). As the use of woody crops for this purpose is becoming more widespread, the commercialisation of this has ensued; forestry industries are vital both for producing fuel and ensuring that forests are sustainably managed (Ramage and Scurlock, 1996). Modified conventional forestry can be used, particularly where hardwood short-rotation crops are grown, which develop fully in 5 to 10 years. Coppicing – where shoots regrow after initial harvesting – can bring about significant biomass accumulations over time and a new crop can be harvested after another 5 to 10 years (Easterly and Burnham, 1996). This is not a new technique but can minimise the costs of operations, as only one planting occurs for many harvests and less demanding management is used (Ramage and Scurlock, 1996). Arable coppice is different, cultivating mainly fast-growing species such as hazel and poplar in developed countries. This may have certain impacts on local ecology, however, and can also be unsustainable due to the economic intensity of operations, as it may be in direct competition with conventional forestry practice; this can nevertheless remediate soil erosion issues (Easterly and Burnham, 1996). Both gasification and combustion technologies are available for processing these crops when they are harvested.

2.2.2.2 C4 and Herbaceous Crops

C4 crops are usually found in tropical or sub-tropical regions, where the photosynthetic processes occurring are distinctly different from the C3 pathway described in the introduction to this thesis. Through enzyme and kinetic labelling experimentation, the C4-dicarboxylic acid pathway was recognised (Hatch and Slack, 1970). During photosynthesis, the CO_2-fixation pathway proceeds by two interconnected cycles; the first includes the carboxylation of phosphoenolpyruvate forming oxaloacetate and the second is the acceptor transferral of a C4 carboxyl from a carboxylic acid (Hatch and Slack, 1970). Some of the reactions that occur during this pathway are, however, similar to those that operate in

the fixation pathways of C3 crops. This mechanism was first discerned due to the 'unusual' chloroplast characteristics and photosynthesis rate in what are now known as C4 plants (Hatch and Slack, 1970). Even though many tropical plants use this pathway, other C4 species do grow elsewhere; many energy crops are, indeed, C4 crops, including sugar cane, maize, sorghum, miscanthus and switchgrass. Due to the locations where these crops are found, some are not suitable for growth in some countries, although they are successful elsewhere. Many herbaceous crops grow in the humid-temperate UK climate, several specifically for processing, which is considered presently. Energy crop production can be advantageous but would usually replace agriculture, thus sites become less intensively managed, less fertilisers are used and the leeching of these would be reduced (González, *et al.*, 2006). Many studies have investigated the use of these crops; González, *et al.* (2006) used pelletised common reed and sorghum in a mural boiler for domestic heating and Gilbert, *et al.* (2009) investigated switchgrass, a C4 energy crop grown in the UK.

2.2.2.3 Crops Grown for Processing

A number of energy crops, such as sugar cane, maize and sorghum are grown, not for the purpose of using them directly as a fuel, but to process them via thermochemical or biological mechanisms to produce biofuels. Key examples are alcohols (methanol and ethanol) and vegetable oil-based fuels. While the feedstocks and properties of these fuels shall be discussed herein, the processes used will be reviewed in the subsequent chapter. The production of alcohols uses fermentation to convert the biomass constituents into the alcohols used as fuels. The main feedstocks to produce ethanol are crops with high sugar, starch or cellulose levels, in particular sugar cane, molasses and cassava (Wereko-Brobby and Hagen, 1996). Of these, sugary crops are favoured as the sugar undergoes direct fermentation to ethanol, though maize and sorghum can be used as well (Ramage and Scurlock, 1996). For methanol, crops with high cellulose levels are utilised. Conventional fuels can be blended with both these alcohols and used as engine fuels (Wereko-Brobby and Hagen, 1996). Vegetable oils can be produced from a range of biomasses, where the main crops are coconut, cotton seed, groundnut, palm, rapeseed, sesame and linseed (Wereko-Brobby and Hagen, 1996). The main components of these oils are hydrocarbon-like fatty acids and glycerol, which have a high energy content and can be used either in place of diesel or blended with it. One issue with this is that engines often become blocked, although esterification of the initial oil can overcome this (Ramage and Scurlock, 1996). Other major ways of enhancing the properties of vegetable oils is to combine it with petroleum or convert them to an alcohol ester (Wereko-Brobby and Hagen, 1996). Their main use is for bio-diesel production for processing into transport fuel, which has recently become available on a commercial scale within the UK.

2.2.3 Properties and Composition of Biomass Fuels and Their Products

2.2.3.1 Calorific Values and Energy Recovery from Biomass-Derived Fuels

The CV of a fuel is the heat produced through completely combusting a known quantity in oxygen and is measured using a bomb calorimeter under specified conditions, where it is assumed that the products of combustion leave the system at atmospheric pressure and temperature (Bone and Himus, 1936; Speight,

2005). Speight (2005) states that this is a 'direct indication' of the heat content and thus the energy value of the fuel. It can be expressed as either gross or net calorific value (GCV and NCV) depending on how the latent heat of condensation of the present water vapour is considered. GCV presumes all vapour is condensed, whereas NCV assumes it is not and it leaves with the other products of combustion. These are sometimes described as the higher and lower heating values (HHV and LHV) respectively. The CV of different biomasses and their derived fuels varies significantly (Table 2.2); some, such as MSW, are fairly low, whereas others, namely bio-methanol and ethanol have excellent energy contents.

TYPE OF BIOMASS/FUEL	GCV (MJ/kg)	NCV (MJ/kg)	SOURCE
Barley Straw	-	16.1	McKendry (2002a)
Bio-Methanol	22.3	19.7	Wereko-Brobby and Hagen (1996)
Cereal Straw	17.3	-	McKendry (2002a)
Danish Pine	21.2	-	McKendry (2002a)
Ethanol	29.7	27.0	Wereko-Brobby and Hagen (1996)
Fir	21.0	-	McKendry (2002a)
Gasification of Wood Chips	-	5.0 MJ/Nm^3	Albertazzi, *et al.* (2005)
Miscanthus	18.5	-	McKendry (2002a)
Miscanthus Giganteus	17.0	-	Adouane, *et al.* (2002)
MSW	9.5	-	DTI (2006)
Olive Residue	20.1		Biagini, *et al.* (2006)
Paper Sludge	5.1		Biagini, *et al.* (2006)
Pine Wood	18.1		Biagini, *et al.* (2006)
Poplar	18.5	-	McKendry (2002a)
RDF	18.6-22.3	-	DTI (2006); Ryu, *et al.* (2006)
Switchgrass	17.4	-	McKendry (2002a)
Wheat Straw	-	17.3	McKendry (2002a)
Willow	20.0	-	McKendry (2002a)
Wood Chips	>16.0		Beekes, *et al.* (2005)
Wood-derived Flash Pyrolysis Oils	23.0 MJ/Nm^3	-	Bridgewater (1994)
Wood-derived Slow Pyrolysis Oils	26.3 MJ/Nm^3	-	Bridgewater (1994)

Table 2.2: Table outlining the variation in CV of various types of biomass and their derived fuel products; if the CV is in the centre, the paper does not define which CV it is.

As stated in the introduction to this thesis, the efficiency of converting solar radiation into chemical energy by plant photosynthesis is extremely low, usually less than 1 %. The inefficiencies that occur during photosynthesis are highlighted in Table 2.3, which shows that whilst 36,000 GJ of solar radiation is readily attainable per hectare each year, only 180 GJ of this, equivalent to 0.5 % of that initially available, is accessible for our use. The inefficiencies in plant photosynthetic processes combined with the inefficiencies in the way we utilise the energy means that the overall energy conversion from the initial solar radiation to our electrical power is incredibly low. Once harvested, there are further energy losses to account for during its use; combustion is not entirely efficient, hence more energy is lost from the system. Other thermo and biochemical conversion processes are also not efficient, thus the energy going into the facility is not the same as what is gained. Due to these losses and inefficiencies, it is essential that energy recovery is maximised. Although conversion efficiencies are often low, many biomass-fuelled processes have higher efficiencies than coal- and oil-fuelled alternatives.

While considering these conversion efficiencies and energy recovery, it is also important to examine the energy balances for forming a fuel – specifically, an analysis of the total energy inputs and outputs. All energy inputs to the system, in terms of fertilisers, transport fuels and processing techniques, need to be quantified and a ratio can be formed when this is also done for the outputs; the product and any waste or heat (Ramage and Scurlock, 1996). This can identify areas where energy inputs need to be or can be minimised and aid the use of recycling wastes and energy recovery mechanisms. These balances thus give an indication of the overall environmental impact of biomass use (Ramage and Scurlock, 1996). In addition, the costs of these inputs and outputs need to be compared to ensure the process is economical. Another factor to influence energy recovery from biomass is the chemical and physical properties of the components, particularly as these determine their value as an energy source (McKendry, 2002a).

INEFFICIENCIES IN PHOTOSYNTHETIC PROCESSES	ENERGY DECREASES	PERCENTAGE OF ENERGY FOR NEXT STAGE
radiation from sun – **initial energy**	36,000 GJ	100 %
only one third is received during growth phase	12,000 GJ	33.33 %
only 20% reaches leaves	2,400 GJ	6.66 %
20% is lost by reflection	2,000 GJ	5.55 %
only 50% is used for photosynthesis	1,000 GJ	2.77 %
only 30% is converted to energy and stored	300 GJ	0.83 %
40% is used to sustain the plant – **final energy**	180 GJ	0.5 %

Table 2.3: The conversion of solar energy into plant biomass, based on the incoming solar radiation for one hectare is 1000 kWh m^{-2} y^{-1}.
Source: Ramage and Scurlock (1996)

2.2.3.2 Composition: Ultimate and Proximate Analyses

Different types of analyses are used to determine fuel composition. An ultimate analysis determines a basic elemental composition, including carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S). Knowledge of this is vital to predict the pollutants that are likely to be produced on combustion, as well as establish the amounts that may form; mercury (Hg) and chlorine (Cl) are thus also sometimes determined. Through this, appropriate abatement or removal strategies can be integrated within the system to deal with problems that may arise. Table 2.4 shows some typical results for biomass fuels.

Proximate analysis determines the constituents, rather than the elemental composition. Table 2.5 shows some archetypal data for a selection of biomass fuels; the ash and moisture are two of the most influential factors on the CV of a fuel and these vary widely between the different biomasses listed. The volatiles and fixed carbon are the combustible materials within a fuel. In addition to ultimate and proximate analyses, full elemental analyses are sometimes required to reveal other problematic elements. Some biomasses have significant alkali metals contents, sodium (Na) and potassium (K) for example; willow, cereal straw and switchgrass contain 15.8 %, 11.8 % and 14.0 % of these respectively (McKendry, 2002a). The ash not only severely affects the CV, but also the amount of solid pollutants (particulates) that are formed on combustion. It is essential for this to be quantified so appropriate measures can be taken to prevent unnecessary releases.

TYPE OF BIOMASS/FUEL	C	H	O	N	S	ASH	SOURCE
Ash	49.7	6.9	43.0	-	-	0.3	McKendry (2002a)
Beech	51.6	6.3	41.4	-	-	-	McKendry (2002a)
Barley Straw	45.7	6.1	38.3	0.4	0.1	6.0	McKendry (2002a)
Hardwood Chips	47.6	5.9	46.3	0.14	0.02	-	Brage, *et al.* (1996)
Hazelnut Shells	51.0	5.4	-	1.3	-	1.3	Biagini, *et al.* (2006)
Miscanthus	48.1	5.4	42.2	0.5	<0.1	2.8	McKendry (2002a)
Olive Residue	51.2	6.7	-	0.8	0.05	1.2	Biagini, *et al.* (2006)
Paper Sludge	24.3	3.4	-	0.5	0.01	47.0	Biagini, *et al.* (2006)
Pine Wood	53.0	6.0	-	0.2	0.08	1.7	Biagini, *et al.* (2006)
RDF	44.3	6.3	28.8	-	-	18.7	Ryu, *et al.* (2006)
Rice Straw	41.4	5.0	39.9	0.7	0.1	-	McKendry (2002a)
Wheat Straw	48.5	5.5	3.9	0.3	0.1	4.0	McKendry (2002a)
Wood Pellets	49.4	6.1	-	1.0	0.7	2.3	Biagini, *et al.* (2006)
Wood-derived Flash Pyrolysis Oils	56.4	6.2	37.1	0.2	<0.01	0.1	Bridgewater (1994)
Wood-derived Slow Pyrolysis Oils	61.9	6.0	29.5	1.05	0.03	1.5	Bridgewater (1994)

Table 2.4: Table of the weight percentages (wt%) of elements in the ultimate analyses for types of biomass used in energy production. Some experiments were performed on a dry ash-free (daf) basis.

TYPE OF BIOMASS	MOISTURE	VOLATILES	FIXED CARBON	ASH	SOURCE
Barley Straw	30.0	46.0	18.0	6.0	McKendry (2002a)
Cereal Straw	6.0	79.0	10.7	4.3	McKendry (2002a)
Danish Pine	8.0	71.6	19.0	1.6	McKendry (2002a)
Fir	6.5	82.0	17.2	0.8	McKendry (2002a)
Hazelnut Shells*	-	78.5	20.2	1.3	Biagini, *et al.* (2006)
Miscanthus	11.5	66.8	15.9	2.8	McKendry (2002a)
Olive Residue*	-	78.4	20.4	1.2	Biagini, *et al.* (2006)
Paper Sludge*	-	50.0	3.0	47.0	Biagini, *et al.* (2006)
Pine Wood*	-	80.6	17.7	1.7	Biagini, *et al.* (2006)
Poplar	45.0	-	-	2.1	McKendry (2002a)
RDF	1.9	69.9	9.8	18.7	Ryu, *et al.* (2006)
Switchgrass	13.0-15.0	-	-	4.5	McKendry (2002a)
Wheat Straw	16.0	59.0	21.0	4.0	McKendry (2002a)
Willow	60.0	-	-	1.6	McKendry (2002a)
Wood Pellets*	-	76.9	20.8	2.3	Biagini, *et al.* (2006)

Table 2.5: Table of the weight percentages (wt%) of substances completing the proximate analyses for different types of biomass used for energy production. * - dry basis.

2.2.4 Environmental Hazards Associated with Biomass Use

One of the most obvious environmental hazards associated with biomass use is the emissions produced on their combustion or treatments. This will be considered in detail in a subsequent chapter. In addition to the detrimental effects of emissions, there are a number of other environmental concerns regarding the growth, harvesting, processing and use of biomass as an energy source; these do not apply to wastes. The main dangers include its competition with food, desertification, soil erosion, deforestation, reduced biodiversity and the loss of genetic resources (UNEP, 1991). Whilst the impact of some can be minimised by ensuring that production and use is sufficiently managed and proceeds in an environmentally-sustainable manner, these can, and have, become extensive problems in certain areas.

2.2.5 The Economics of Producing and Using Biofuels

The main influences on the overall costs of producing a biofuel are the building and set-up costs, the price of the initial feedstock, staff wages and operating time. In countries that process biomass to commercially manufacture biofuels, the economic viability is unfortunately directly related to the price of fossil fuels. It is particularly difficult to compete with these industries if there are fluctuating oil prices, thus there is no financial advantage to the employment of these systems, unless substantial governmental subsidies are provided (Wereko-Brobby and Hagen, 1996). The economics relating to the production of alcohol fuels, for example, varies noticeably between countries; in most cases, the costs of constructing and using processing plants is unknown, due to lack of experience and expertise and thus predictions are difficult (Wereko-Brobby and Hagen, 1996). Due to the often unfavourable economics of production, these costs have to be passed on to the consumers, so using biofuels can be expensive. The cost of vegetable oils, for example, is usually significantly higher than for comparable fossil fuels. Again, governmental initiatives, such as funding or subsidies, are required to encourage the use of these more environmentally-friendly fuels. Recent legislation is trying to enforce such projects through implementing directives, such as the EU Biomass Action Plan, in which fines are incurred if renewable targets are not met, consequently promoting the use of renewable fuels in a variety of sectors.

2.3 LEGISLATION GOVERNING WASTE MANAGEMENT AND RENEWABLE ENERGY

Legislation, on a national and international scale, is vitally important in the management and control of waste disposal and energy generation. Waste management is necessary to ensure that the waste produced is handled in a responsible manner; policies focusing on the issues that arise from the management of the vast amounts of waste produced include the Landfill Directive and Waste Management Licensing, which apply to the management of SMC. The legislation concerning energy and its impacts is varied and continually being developed; this includes those relating to renewable energy, such as Earth Summit outcomes, IPPC Directive, EU Renewable Energy Policy and EU Common Energy Policies. Further policies have been devised to focus exclusively on energy generated from biomass resources, including the EU Biomass Action Plan and legislation that promotes their use, such as the Climate Change Levy and the Non-Fossil Fuel Obligation. A specific policy relating to the reuse of waste as an energy source is the Waste Incineration Directive (WID), which concerns the reuse of SMC and coal tailings as a source of energy. In this section, the primary policies relating to the issues at hand are considered; the Landfill Directive, Waste Management Licensing, WID and the Renewables Obligation Order.

2.3.1 The Landfill Directive

The Landfill Directive (1999/31/EC) was introduced to prevent, or at least minimise, detrimental health and environmental effects caused by waste landfilling (DEFRA, 2005). The policy changed the way sites are managed and set targets to reduce the amounts of MSW disposed in landfills; the ultimate goal is that

by 2020, biodegradable MSW sent to landfill will be reduced to 35 % of that in 1995 (DEFRA, 2005). The primary mechanism is to alter the amount of waste going to landfill by moving it up the hierarchy (Figure 2.2), leading ultimately to a permanent change in the way it is disposed. As seen in this conceptual framework of waste management strategies, reduction is the most efficient, eliminating the source of the problem; reusing and recycling are also important. Energy can be recovered from waste collected by the council, and is already carried out in locations, such as Sheffield, as previously discussed. Landfill should therefore be the last resort in dealing with wastes. Energy should hence be recovered from wastes, such as SMC and coal tailings, where other options are not suitable or practicable. The Environment Agency will ensure the implementation of this directive and control landfill regulation.

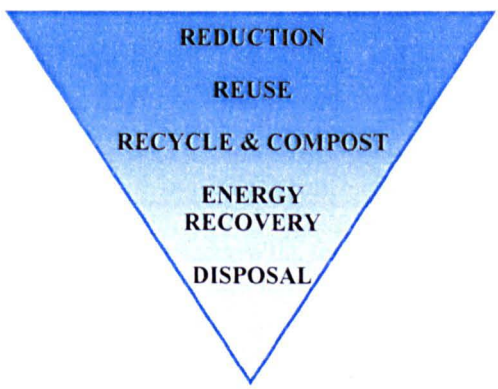


Figure 2.2: The ideal waste minimisation hierarchy. The relative width of the triangle at each method reflects the importance the process should have in society; conversely, this is not the case.

2.3.2 Waste Management Licensing

A waste management license is a legal document, issued on application to the majority of facilities which deposit, store, treat or dispose of waste under section 36 of the Environmental Protection Act 1990 (DEFRA, 2007). Its primary purpose is to ensure that the health of populations and the local environment and amenities are not adversely affected by any waste management processes carried out at these sites or plants (Environment Agency, 2007). There are two main types of license, site licenses and mobile plant licenses, which can be obtained from the relevant environmental regulator, the Environment Agency for example for those in England and Wales, although exemptions apply to some, particularly small-scale activities (DEFRA, 2007). Such a license would be required by any company that wishes to transport, pelletise and use the SMC and/or coal tailings for the purpose of energy recovery.

2.3.3 Waste Incineration Directive

This EC-wide directive (2000/76/EC) concerns the environmental implications of hazardous and non-hazardous waste incineration and co-incineration and is further to the legislation outlined in previous Municipal Waste Incineration Directives (89/429/EEC and 89/369/EEC) (DEFRA, 2006a). Implemented in 2002-2003, WID intends to prevent, or at least limit the detrimental environmental influences of waste incineration, primarily through regulating emissions, see Table 2.6, and monitoring installation operations (DEFRA, 2006a; NetRegs, 2007). This works with the IPPC, Integrated Pollution Prevention and Control

Directive (96/61/EC), to manage industrial installations, including those in the energy sector. The main aim is to provide a more holistic approach, by integrating the reduction in energy consumption and related emissions into the wider context of environmental management (Envirowise, 2006). This is achieved by introducing a minimum standard for technical procedures and tight control of operations. WID applies to all who combust or co-fire solid or liquid wastes in a technical unit, for disposal or energy recovery (NetRegs, 2007). The thermal treatment of SMC and coal tailings must thus conform to WID.

EMISSION	AVERAGE EMISSION LIMIT (mg/m^3)	
	HALF-HOURLY	DAILY
Total Dust	10 – 30	10
HCl	10 – 60	10
HF	2 – 4	1
CO	150	50
SO_2	50 – 200	50
NO and NO_2	200 – 400	200 – 400
Heavy Metals	0.05	0.05
Dioxins	0.1ng I-TEQ/Nm^3	0.1ng I-TEQ/Nm^3

Table 2.6: Emission limits for incineration under WID, for dry gas at 273 K, 101.3 kPa and 11 % O_2. Source: DEFRA (2006a)

2.3.4 The Renewables Obligation Order

The Renewables Obligation Order of 2002 sets targets to licensed energy providers to increase the amount of electricity generated from renewable resources; for 2015-2016, the target is 15.4 %. Each MWh generated from a renewable source results in the issuing of a Renewables Obligation Certificate (ROC). Biomass and biomass-derived energy play a major part, where incineration and other treatments, such as pyrolysis, gasification and anaerobic digestion would be eligible to qualify. However, as of April 2009, 25 % of the co-fired biomass must be an energy crop, and thus the SMC used herein would no longer qualify, unless co-fired with, for example, hazel or switchgrass. Furthermore, co-firing with coal tailings, which are fossil-fuel based, would cease to be eligible after 2016. Despite this, the Renewables Obligation coupled with the Climate Change Levy – a support mechanism, whereby renewable energy and CHP are exempt from charges enforced on other energy sources – provide a monetary support mechanism to the renewable energy industry.

2.4 SPENT MUSHROOM COMPOST

2.4.1 Formation of Spent Mushroom Compost

The formation of the initial compost used for mushroom growth is a well understood and non-contentious process, which takes place in four stages, depicted in Figure 2.3. Although the second and third stages (Phase I and II) are both composting phases, they are distinctly different, as shall be seen. When Phase III is complete, if it is needed, the compost that has been produced is sold to mushroom growers for cultivation purposes; this entails a variety of further processes, which shall be discussed herein. After the optimum number of mushroom batches has been cultivated, the now spent compost is removed and

requires disposal (Williams, *et al.*, 2001a). The whole process, from compost formation to compost disposal, can take up to 15 weeks. The many stages within this all require a variety of specific conditions to ensure that the processes are completed to a satisfactory degree (Volk and Ivors, 2001).

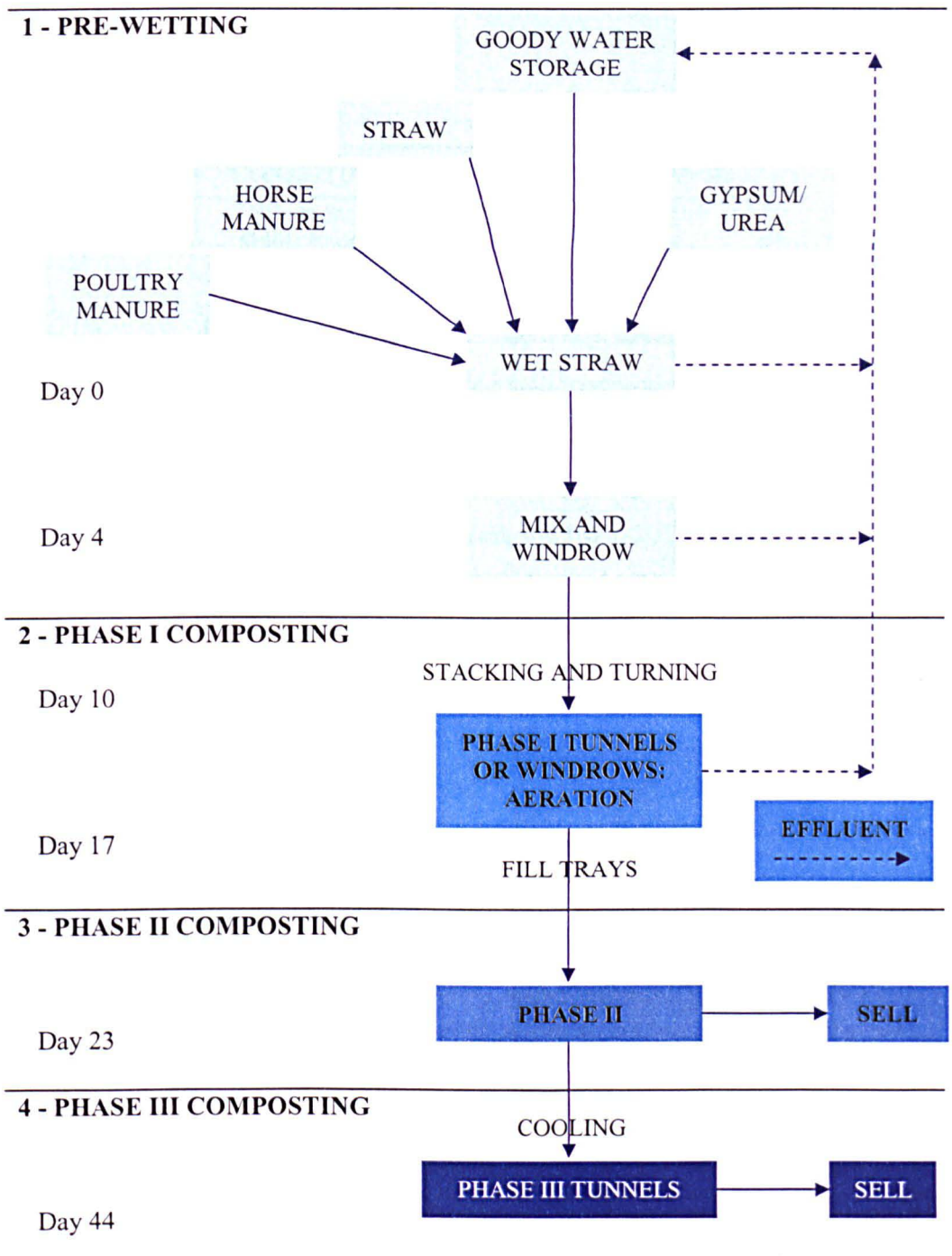


Figure 2.3: A chronological flow diagram of the formation processes of the initial compost used for mushroom cultivation.
Source: Adapted from DEFRA (2006b), with additional information from Iiyama, *et al.* (1994)

2.4.1.1 Stage 1: Pre-Wetting

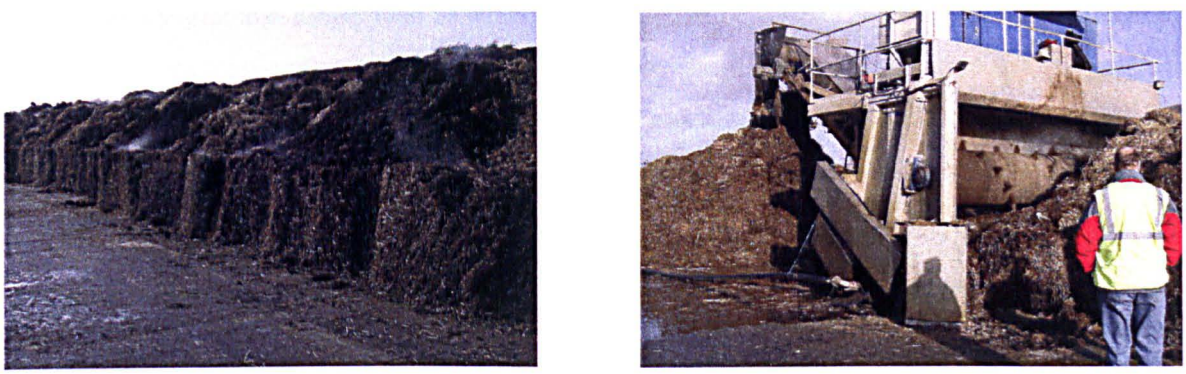
In the first step of compost formation, all the substances that make up the final compost are combined. Although the composition can vary greatly between different producers, some general percentages of these constituents are shown in Table 2.7. Usually, the raw materials are quite dry and thus (wheat) straw

is wetted until the appropriate moisture content is reached. The water in this stage and throughout the following stages is referred to as 'goody' water, which is continuously recycled, as shown in Figure 2.3. This is then mixed well with some or all of the following to produce a uniform substance: gypsum (calcium sulphate), horse manure, stable bedding, poultry litter, peat, lime, molasses and other sugars, urea, activators and a number of optional substances, such as other agricultural wastes (Iiyama, *et al.*, 1994; DEFRA, 2006b).

CONSTITUENT	PERCENTAGE RANGE
Wheat Straw	40-45 % (dry weight)
Stable Bedding	20-25 %
Poultry Manure	10-15 %
Gypsum	5-10 %
Optional Components	10-15 %

Table 2.7: Table showing the general composition of the initial components that form mushroom compost. Source: Iiyama, *et al.* (1994)

Substitutes for many of these can be added, which may comprise fibrous materials such as dry or spent brewers grain, hay, cotton seed hulls and corncobs (Volk and Ivors, 2001). This blend is mixed and piled up, then thoroughly mixed again using appropriate machinery, as seen in Figure 2.4. At this stage, more water is added if necessary. After this final mixing, the combined materials are moved to windrows to start the next stage of the process – the two composting phases.



(a) (b)

Figure 2.4: The raw substances in the mushroom compost and mixing: (a) heaps of pre-wetted straw; (b) the machine carrying out final mixing before Phase 1 composting.

2.4.1.2 Stage 2: Composting Phase I

There are two distinct composting stages. The first occurs after the initial mixing, where the mixture is stored outdoors and turned further to regulate the temperature to about 50-60 °C; this can be done in silos or in a yard, known as windrows (Figure 2.5). These windrows are typically 1.8 m wide and 2.0 m high (DEFRA, 2006b). Thermophilic bacteria cause temperature fluctuations, which grow rapidly and produce the heat necessary for both this stage and the next. This allows aerobic conditions to develop over several days, sometimes up to two weeks. It is generally not left for more than three days between mixing; here, the main aim is to initiate microbiological decomposition (Williams, *et al.*, 2001a; DEFRA, 2006b).

Figure 2.5: Phase I composting taking place in windrows. The raw materials (straw) are in the background.

Once the compost is thoroughly mixed, it is transferred inside, to bunkers for aeration, which can be done by using either ventilation or mechanical movement – forced aeration (Figure 2.6). The oxygen content can be monitored to ensure levels are sufficient, generally between 3 % and 12 % (DEFRA, 2006b). The temperature reached in this stage is about 80 °C, all produced by microbial action. Any drainage effluent produced by this process is returned to the compost to adjust the moisture content, where required; this is goody water recycling. This stage is finished by removing it from the bunkers and allowing it to cool (Figure 2.7). When the material is workable and can hold sufficient moisture, the first composting phase is complete, which is indicated by even, dark brown compost with ammonia odours, suggesting sufficient decomposition of the initial materials has taken place (Volk and Ivors, 2001). The colour change indicates that bacteria and fungi, such as actinomycetes, have performed their function and successfully changed the constituents to those which are useful for providing nutrients to mushrooms (Iiyama, *et al.*, 1994). If aerobic conditions are not maintained and an anaerobic environment is allowed to develop in the centre of the compost windrow, decomposition is impeded and a lighter, more odorous material is formed (DEFRA, 2006b).

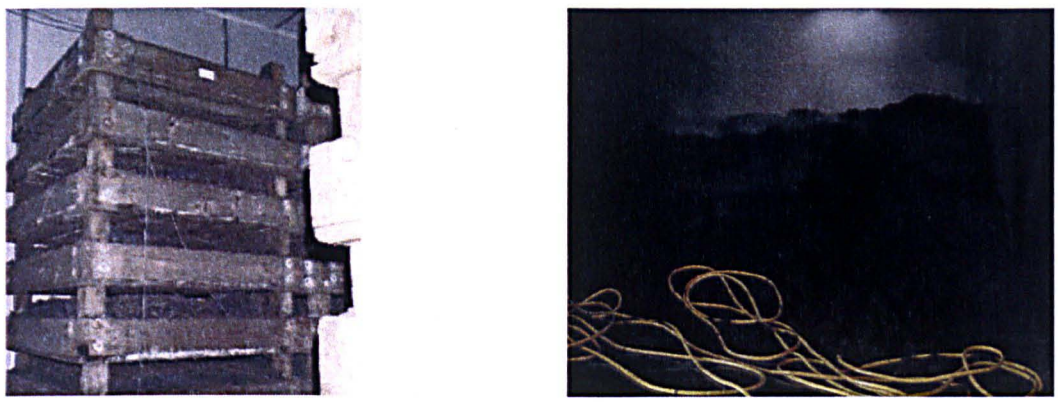
Figure 2.6: Aeration hole in the floor of the bunker for Phase 1 composting.

Figure 2.7: Steam being released during the cooling stage at the end of Phase 1 composting.

2.4.1.3 Stage 3: Composting Phase II

This composting phase involves the pasteurisation and conditioning of the material produced from Phase I, which also both occur in highly aerobic environments. The key distinction between Phases I and II is

the degree of control over the conditions (Volk and Ivors, 2001). The material is placed where the floor is slatted, either in insulated trays and stacked inside or placed in insulated tunnels, in a closed environment where the conditions can be carefully manipulated (Figure 2.8).



(a) (b)

Figure 2.8: Phase II composting, where the compost from Phase I is placed in (a) wooden trays or (b) in tunnels for the pasteurisation and conditioning stages.
Source: (a) Volk and Ivors (2001)

Pasteurisation involves controlling the temperature to 60 °C for at least two hours, usually using steam. This eliminates any insects, pathogens or other pests that may have survived Phase I and also converts the many nitrogen-containing species present into nutrients, mainly proteins, that are useful for mushroom cultivation in later stages (Volk and Ivors, 2001; DEFRA, 2006b). Some microbes, however, do survive this phase, which is imperative, as these further aid nitrogen-conversion mechanisms; some of these also impede the growth of rival fungi, which could influence mushroom yields (Iiyama, *et al.*, 1994). The temperature can then be reduced to about 46 °C using cool air for the conditioning process to occur, which reduces the ammonia levels to about 10 ppm using oxygen, as it can be fatal to the mycelium placed in the compost later (Williams, *et al.*, 2001a). If the ammonia is not converted, it can be blown off instead. This conditioning normally lasts about a week (Iiyama, *et al.*, 1994). Lastly, the temperature of the compost is reduced further to between 20 to 30 °C. After this, the compost is said to be 'selective' for mushroom cultivation (Maher, *et al.*, 2000).

2.4.1.4 Stage 4: Operations

Phase III composting may or may not occur, as it is simply further processing. If it does, it may include early mushroom germination (DEFRA, 2006b). After the compost is formed, "spawning, casing, pinning, and cropping" occur (Volk and Ivors, 2001). Typically, the mushroom compost is delivered to growers pre-spawned, where mycelium are already combined with the compost using specific machinery, such as a spawning hopper. This is the first process to take place after compost formation. The mushroom spawns or mycelium are placed on grains, which are then mixed with the compost. The spawns are acquired from specific manufacturers and few compost producers or mushroom growers use their own mushroom spawns. This pre-mixed substance is placed in polyethylene sacks, usually 20 kg, which are sold and delivered to the mushroom growing farms (Maher, *et al.*, 2000). After spawning, it is vital that

the conditions remain fairly constant, so the humidity and CO_2 levels are monitored; temperatures are also maintained at 24 °C.

The pre-spawned substrate is placed into trays at the farm and the top is flattened. A peat casing layer (Figure 2.9), which may also contain some limestone, is added to the surface and has a distinctly different composition and function to the substrate layer (Williams, *et al.*, 2001a). Usually 4-5 cm in depth, as seen in Figure 2.10, this casing provides anchorage for the developing mushrooms and moisture due to its good water retention, although no nutrients originate from here (Volk and Ivors, 2001). Furthermore, it must be porous to allow mycelial respiration and should resist breakdown from frequent watering (Noble and Dobrovin-Pennington, 2005). The casing layer is clean but not sterilised like the substrate.

Figure 2.9: The peat/lime casing layer, delivered to the farms separately from the substrate.

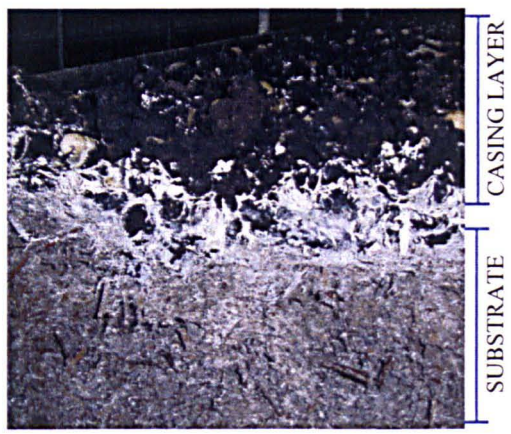


Figure 2.10: The peat/lime casing layer added to the substrate surface for mycelium colonisation.

Once the compost has been prepared, mushroom cultivation and growth can begin. Complete mycelium colonisation, seen in Figure 2.10, takes 2-3 weeks, dependent on the environment in which they are kept. Initial mushroom growths are known as primordial or pins (Figure 2.11), and once the casing layer is reached by these, the temperature is reduced to 16-18 °C and the CO_2 concentration to 0.08 % throughout the growth stage (Volk and Ivors, 2001). Control of compost moisture is also important; the casing should be watered 2-3 times a week. Growth takes up to 4 weeks, until they reach a size sufficient to harvest (Figure 2.12), upon which they are hand-collected. The life cycle of mushrooms, depicted in Figure 2.13, shows the developmental and growth stages, discussed above.

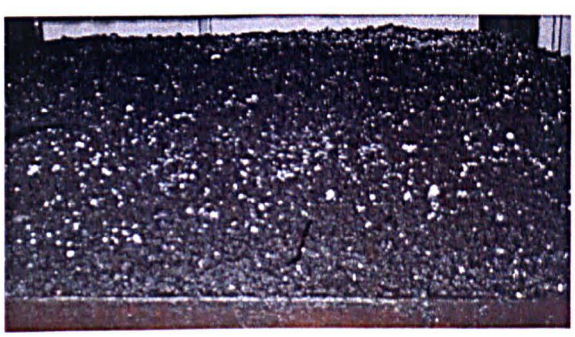


Figure 2.11: *Agaricus bisporus* pins. Source: Volk and Ivors (2001)

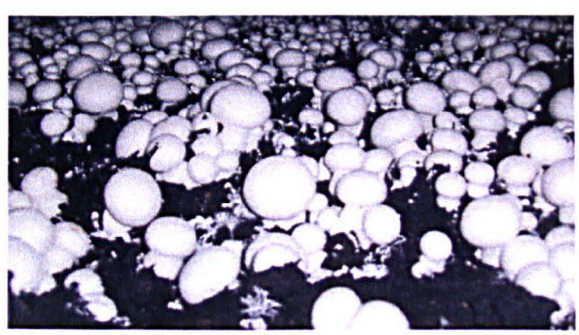


Figure 2.12: A crop of *Agaricus bisporus* ready to harvest.

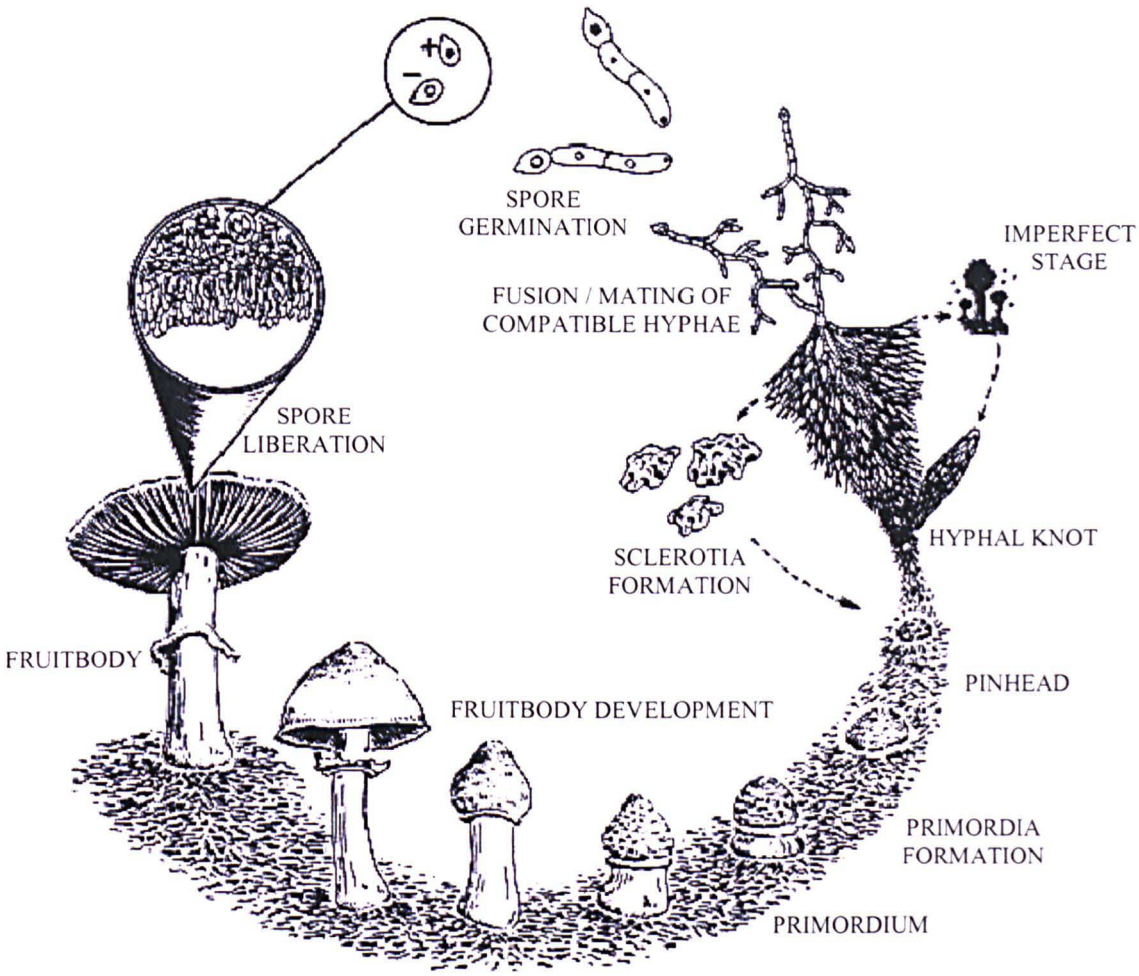


Figure 2.13: The life cycle of mushrooms.
Source: Stamets (1995)

Four batches of mushrooms are grown consecutively in the compost before it is replaced; smaller quantities of mushrooms are produced in each consecutive batch or 'flush' (Volk and Ivors, 2001; Williams, *et al.*, 2001a). A large variety of mushroom species grown are on a commercial basis, the most common are from the large *Agaricus* genus, such as the *bisporus* species. They produce white button mushrooms, crimini mushrooms or Portobello mushrooms, depending on the length of time they are grown, and hence the size they reach (Figure 2.14). Other types of common edible mushrooms, for example shiitake and oyster mushrooms, are not produced in this way as they are primary decomposers and grow on wood instead; *Agaricus* mushrooms are secondary decomposers, using material previously broken down by other fungi and bacteria, and therefore require compost (Volk and Ivors, 2001).

Figure 2.14: The various stages in the development of *Agaricus bisporus*; on the left is the white button mushroom, in the centre is the crimini and on the right is the large Portobello mushroom.
Source: Volk and Ivors (2001)

2.4.1.5 After Mushroom Cultivation

Subsequent to the cultivation and harvesting of the third or fourth mushroom crop, the remnants of mushrooms in the compost are 'killed off' or 'cooked out' (Figure 2.15). This entails using either steam or a dilute formaldehyde solution at high temperatures to sterilise the now spent compost and prevent further mushroom growth (Williams, *et al.*, 2001a). The SMC, which comprises both the substrate and its casing, is now nutritionally-exhausted; it can then be removed, upon which the containers are washed, disinfected and await new compost for further mushroom yields. The SMC produced in this process can then either be utilised in some way or requires disposal; unfortunately, there do not appear to be any entirely environmentally-friendly ways of disposing of this material. In some cases, the disposal is in the form of landfilling, which has obvious detrimental effects on the environment. In certain regions of Ireland, there are no established disposal techniques and SMC removal from farms is therefore often environmentally degrading and probably illegal; as Williams, *et al.* (2001a) report, it is not unusual to find sacks of SMC simply dumped at the roadside (fly-tipping) or in abandoned quarries, particularly in Tyrone, Monaghan and Armagh, three of the major mushroom producing counties. In other areas, it is spread over agricultural land, although as discussed below, this also has considerable environmental implications. There are, however, a number of uses for this substance, which aim to divert this material from landfill sites and other places that may have negative environmental impacts.

Figure 2.15: A sample of SMC which has been heated using steam to be 'cooked out'.

2.4.2 Quality and Quantity of Spent Mushroom Compost

2.4.2.1 Production Rates of Spent Mushroom Compost

It is thought that for every 1 kg of mushrooms produced, 5 kg of SMC will be formed as a by-product (Williams, *et al.*, 2001a; Lau, *et al.*, 2003). As mushroom production is commercial and large scale, thus producing thousands of tonnes of mushrooms each year, the amount of SMC that is also formed is vast. Using this ratio, it is possible to estimate SMC generation where mushroom production data is available (Table 2.8), as actual SMC generation data is only available for a few countries. As can be seen, it is thought that many countries produce significant amounts of mushrooms and thus SMC. Although mushroom and SMC production are generally stable, China in particular has shown rapid increases in the engenderment of both over the last 10 years. The trend, however, is starting to wane and a primary cause of this may be the issues related to SMC disposal. If this trend continues, the use and disposal of SMC

will become increasingly problematic and therefore even higher on the agenda of mushroom farmers. In Europe, SMC production varies considerably (Table 2.9).

COUNTRY	MUSHROOMS PRODUCED (tonnes)	ESTIMATED SMC PRODUCED (tonnes)
Australia	46,270	231,350
Belgium	43,000	215,000
Canada	84,680	423,400
China	1,360,500	6,802,500
Germany	65,000	325,000
India	48,000	240,000
Italy	94,150	470,750
Japan	64,000	320,000
Korea (N and S)	31,300	156,500
Poland	130,000	650,000
USA	391,000	1,955,000

Table 2.8: Estimated SMC generation based on mushroom production data by country for 2004. Source: FAO (2006)

COUNTRY	TONNES
Netherlands	700,000
Spain	320,000
Ireland	273,000
France	250,000
Israel	15,000
Greece	10,000

Table 2.9: Table showing the actual annual production rates of SMC in a range of European countries. Source: Mikkelsen, *et al.* (2006)

The mushroom industry is of great importance both in Northern Ireland and the Republic; combined, they produce 273,000 t/a of SMC. Williams, *et al.* (2001a) reported that in the main five border counties of Ireland, approximately 190,000 t/a is produced, with Monaghan the primary producer (Figure 2.16). This county alone produces 70,000 t/a – a significant contribution to the border counties total and Ireland's overall generation. Of the SMC available in the border counties identified, Williams, *et al.* (2001a) assume that 100,000 t would be available for energy recovery, although at present most goes to either fertilise local land or is disposed of. Spain and the Netherlands both produce significantly more SMC, as shown in Table 2.9, and therefore it can only be assumed that the problem of disposal here is greater, unless its uses are vast. France also produces much SMC per annum. In the UK, 200,000 t/a are generated; mushroom producers have been identified on Figure 2.17.

The SMC used in this investigation is sourced locally, from a farm located near Whitley in Yorkshire; this is a large mushroom farm and is therefore a significant producer of the SMC generated in the UK. This mushroom farm is also identified on Figure 2.17. Once the materials are prepared, the farm obtains the locally-produced initial compost and casing layer from a composting facility near Bawtry; the substrate contains a mixture of straw, gypsum and chicken litter, while the casing layer, which is used on the surface, is composed of peat and lime. The amounts of compost, mushrooms and SMC produced are

given in Table 2.10. The process at this facility is the same as that described in Section 2.4.1, where the phases of composting the initial materials are followed by spawning and then mushroom cultivation and harvesting. The initial compost is packaged and transported to the mushroom farm after the spawning stage, and when the compost is spent it is taken to a local farmer, where it is stored until it is needed for fertilising the surrounding farmland or taken for disposal. The mushrooms produced are packaged and taken to large supermarket chains; it is only if there is a particularly large crop that they are sold at local farmers' shops or markets.

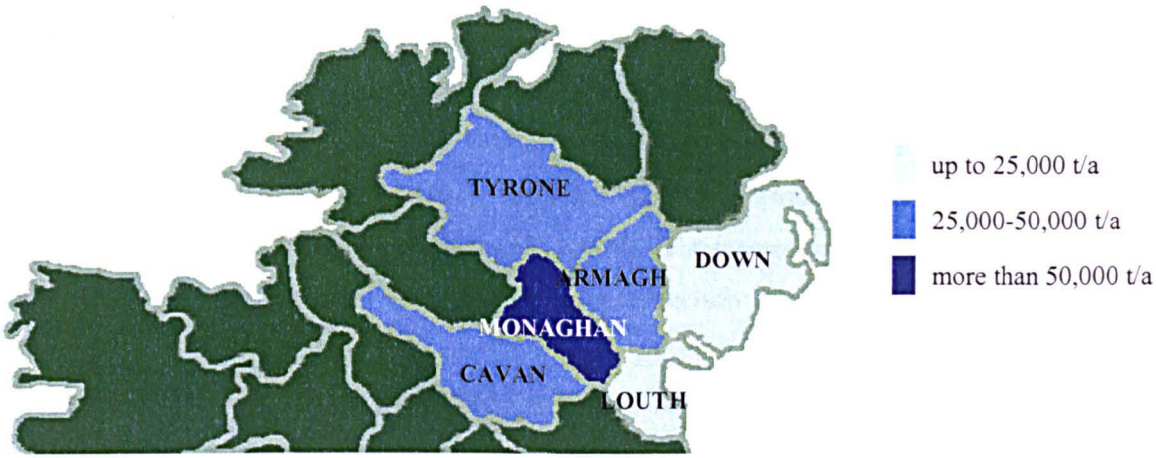


Figure 2.16: Annual SMC production in Northern Ireland and the border counties.
Data source: Williams, *et al.* (2001a)

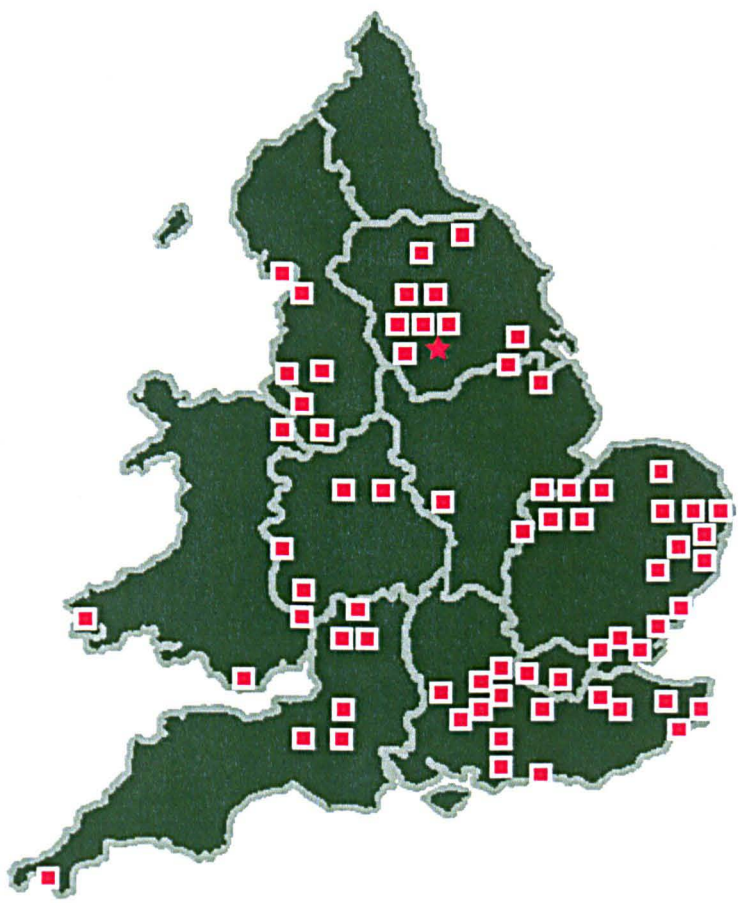


Figure 2.17: Locations of the major mushroom farms in England and Wales.
★ Source of SMC for the investigation

SUBSTANCE PRODUCED	AMOUNT (t/wk)
Initial Compost	1500-2000
Mushrooms	50-60
SMC	150-200

Table 2.10: Table of the amount of compost produced and the amounts of mushrooms and SMC generated at the composting facility and the mushroom farm from which the resources for this investigation come.

2.4.2.2 Composition and Properties

The composition of SMC varies from sample to sample due to differences in their production, disparity in the materials used and amount of casing layer added, as well as the quantity of moisture included during mushroom growth (Ball and Jackson, 1995; Williams, *et al.*, 2001a; McCahey, *et al.*, 2003). Whilst the properties of the compost produced from the same yard may be very similar, the variability in the composition of SMC increases dramatically with the number of sources, particularly the total and available phosphorus and potassium (Jordan, *et al.*, 2008a). The inconsistencies in nutrient content of the material between the suppliers are of specific importance, especially if it is later to be used as a fertiliser.

The initial components of the compost were presented in the previous section, although the final composition of SMC is obviously different, due to the decomposition of the materials, the removal of nutrients during mushroom growth and the addition of the casing layer. The general composition of some SMC samples is shown in Table 2.11. As can be seen, the moisture content is high, often 60-77 % on an as-received (ar) basis; this is one of the primary factors controlling the CV as it determines the energy obtainable from the fuel, as considered below (Williams, *et al.*, 2001a; McCahey, *et al.*, 2003). The ash, volatiles and fixed carbon contents do not vary as much and are therefore less likely to negatively impact combustion. The ash content is quite high and Iiyama, *et al.* (1994) suggest that sand, soil and stone are often present in the compost and may contribute to the significant proportions of ash.

PROXIMATE	%
Total Moisture (ar)	60-77
Ash (ar)	6-13
Volatile Matter (ar)	14-23
Fixed Carbon (ar)	3-5
Ash (dry)	27.0-33.4
Volatile Matter (dry)	57.0-59.1
Fixed Carbon (dry)	9.6-14.9

ULTIMATE (dry)	%
Carbon	33.7-37.3
Hydrogen	3.7-3.9
Nitrogen	1.8-2.9
Oxygen	24.4-28.0
Sulphur	1.25-2.94
Phosphorous	0.55-1.37
Chlorine	0.43-0.55

Table 2.11: Tables of the composition (proximate and ultimate analyses) of SMC on 'as received' (ar) and dry bases; values shown are the range for a number of representative samples across Ireland. Source: Williams, *et al.* (2001a)

The CV of the SMC is one of the most important properties, as it will be used as a fuel. As shown in Table 2.12, on a dry basis it is thought to be comparable to sewage sludge, MSW and other waste fuels considered in Table 2.2 (McCahey, *et al.*, 2003). The importance of this is that sewage sludge and MSW are already effectively used as fuels (Williams, *et al.*, 2001a). Furthermore, sewage sludge has a high moisture content and thus the moisture contained in the SMC may not be as problematic as first thought if

it can be dried. Energy recovery from this waste-product has been tested and was found to be appropriate, through combustion in a bubbling fluidised-bed combustor (McCahey, *et al.*, 2003).

BASIS	GCV (MJ/kg)
As Received	3.2-4.6
Dry Basis	12.1-13.7
Dry Matter	9.0

Table 2.12: Table of typical GCVs for SMC from a range of representative samples across Ireland. Source: Maher, *et al.* (2000) and Williams, *et al.* (2001a)

SMC, as suggested by Maher, *et al.* (2000) and seen above, demonstrates some key properties of other organic wastes; these include its high moisture and organic matter content, in addition to the low bulk density and moderate although uneven distribution of plant nutrient levels (Table 2.13). These data regarding the composition of various SMC samples, above and below, can also be used as a comparison to the results for the material characterisation phase of this investigation. Due to these levels of nutrients, SMC is often used as a fertiliser and is even sold in garden centres as compost for bedding plants; the nutrients available for mushroom growth, however, have already been exhausted.

CONSTITUENT (mg/l)*		MEAN
Available Nutrients	**pH**	6.6
	NO_3-N	62
	NH_4-N	49
	P	31
	K	2,130
	Na	253
	Cl	118
Total Nutrient Content	**N (g/kg DM)**	25.5
	K	25.0
	Ca	72.5
	Mg	6.7
	S	15.9
	Na	2.67
	Fe (mg/kg DM)	2153
	Mn	376
	Cu	46
	Zn	273
Other Constituents and Properties	**Bulk Density (g/l)**	319
	Dry Matter (%)	31.5
	Ash (%)	35.0

Table 2.13: Available and total nutrients from a number of SMC samples from Ireland – dry matter (DM).
* mg/l in a 1½ distilled water to 1 SMC volume extract.
Source: Maher, *et al.* (2000)

2.4.3 The Potential Use of Spent Mushroom Compost

The potential use of SMC as a fuel has not been widely investigated, as demonstrated below, as just a few papers concerning this have been written. The alternative potential uses of SMC have however been studied in-depth and these vary widely; the most important factor in any use of this waste is that it is diverted from landfill, as this has a multitude of severe detrimental effects on the environment, as do the

other disposal mechanisms. Further use of SMC for energy recovery will ensure even more can be utilised in an environmentally-sustainable way.

2.4.3.1 Use as a Renewable Fuel

Only a few previous studies into the investigation of SMC as a renewable fuel have been conducted. Highly specific studies have been performed by Williams (2001), Williams, *et al.* (2001a) and McCahey, *et al.* (2003). A demonstration project using SMC in a CHP station has also been completed (BioMatNet, 2004). In an earlier project with much wider scope, SMC was also considered as a fuel for incineration (Maher, *et al.*, 2000). This was the first study in this area and investigated a wide range of SMC management-related topics, one of which was incineration. The conclusions from this were that it could provide a continuous fuel, as the industry works all year round, although drying or mixing with drier materials was needed as the high moisture content meant that it failed to ignite. The testing of the CV, as reported above, showed promising results that were comparable to other fuels. The specific application for this fuel was for the cement industry; this was found to be ideal as the continuous energy needs could be met and the waste heat produced could be used to pre-dry the SMC fuel. Furthermore, it was found that the Mg and Ca components of the SMC could be used as raw materials in the cement and the alkali cycle could also balance the P in the SMC. Most importantly, this could be carried out with little economic investment and without degrading cement quality.

The later study by Williams, *et al.* (2001a) and their follow-up investigations (Williams, 2001; McCahey, *et al.*, 2003) proposed that SMC can be combusted in a bubbling fluidised-bed, creating superheated steam to generate power with high efficiency and recover the heat. This was compared to tests using a stoker-fired chain grate boiler system, which was less successful due to the moisture content. Within their research, the availability and suitability of this substance were evaluated and sites were identified where assessments of the combustion could be carried out. Williams, *et al.* (2001a) also identify what they term 'auxiliary fuels' – fuels, such as natural gas, that can be co-fried with SMC, either initially, only during the start-up phase of operations, or continuously. When only used to begin with, this fuel promotes drying of the SMC, enabling greater energy recovery to be achieved, by pre-heating the combustion air. However, as the moisture content, indicated above, is high and significantly variable, this may necessitate the use of an auxiliary fuel throughout the duration of combustion, unless drying is used.

A subsequent investigation on the use of SMC as a fuel has been undertaken (BioMatNet, 2004). This project sought to provide energy in a 28 MW CHP plant in Monaghan, the county producing the most SMC in Ireland. The aims were to improve the future prospects of the industry through providing an environmentally responsible waste management strategy and to avoid the environmental degradation of landfill and spreading SMC on agricultural land. The SMC, poultry litter and a potential third biomass (wood chips) will be used in a spreader stoker boiler or bubbling fluidised-bed with a steam turbine generator, to produce 22.5 MW of renewable energy in the form of electricity for the national grid.

When SMC is used as an energy resource, its combustion leads to the production of ash, about 10 % of its original volume, in addition to what it already contains. It may not be necessary to find a disposal route for this, however, as the ash could be utilised. Russell, *et al.* (2005) have completed a preliminary investigation into the use of SMC ash (SCMA) as an activator for pulverised fuel ash (PFA) in the cement industry. The ash produced can be utilised as a chemical activator to enhance the pozzolanic reactivity of PFA, which has replaced Portland cement due to its superior properties, even though shortly after manufacture, its strength development is slow. SCMA and PFA mixtures ensure rapid early strength improvements, although it is too soon to investigate the long-term implications of its use. With this in mind, it is possible that the SMC waste produced by the mushroom growing industry could be used to produce a renewable, practical fuel, especially when combined with other fuels, such as coal tailings.

2.4.3.2 Agricultural and Horticultural Uses

There are many other potential uses for SMC; these can generally be classified as agricultural, horticultural or industrial, where the latter often employs complex processes. A range of purposes of SMC utilisation will now be considered; many of these were reported in the 4th International Conference on Mushroom Biology and Mushroom Products by Rinker (2002) and described in Maher, *et al.* (2000).

There are many agricultural and horticultural applications of SMC; it can be used as a fertiliser in a number of situations, including mushroom cultivation, as well as being useful for animals, in terms of environmental enrichment and fodder. Rhoads and Olson (1995) and McCahey, *et al.* (2003) discuss its use as an agricultural fertiliser, simply by spreading it over land, which results in enhanced crop growth, at a more rapid rate. The optimum application was found to be 20 t/acre and was particularly beneficial when used immediately before planting, resulting in yields up to 57 % higher than if the SMC was applied 12 months before planting. The increases in crop yield were attributable to higher nitrogen levels available for growth. Courtney and Mullen (2008) also investigated the use of organic residues, such as SMC, in agricultural applications as both a disposal method and a source of nutrients. They compared the impacts of the land application of SMC, forced aeration compost and an inorganic fertiliser on the quality of soil and the growth of *Hordeum vulgare* – barley. Both organic materials increased soil nutrient levels, where SMC was thought to be more effective, and did not result in elevated Zn or Cu concentrations. This particular use, however, can have detrimental effects on local watercourses, as phosphorous and nitrates leach into river networks causing eutrophication (Williams, *et al.*, 2001a). This is the process whereby nutrients enrich the water enabling the plants present to grow excessively, particularly algae; this in turn reduces the dissolved oxygen content of the water, inhibiting the growth and development of organisms that require oxygen, such as fish. In extreme cases, nothing except the algal blooms survive. As the industry has become more intensive, the SMC available for this considerably exceeds its demand.

The use of SMC as a fertiliser for shrubs in containers was therefore evaluated (Chong, *et al.*, 1994). It was found that for three of the four deciduous shrubs investigated, growth was 20 % greater in peat-based

SMC and growth was better for those where SMC was derived from straw-bedded horse manure. Gent, *et al.* (1998) investigated the effect of fumigation on potato fields with one of four materials, including SMC; vegetation growth increased with SMC additions and was thought to be related to the nitrogen and phosphorous concentrations in the leaves. SMC and fumigation did not however have a beneficial effect.

Maher, *et al.* (2000) discuss many agricultural aspects of SMC, specifically its use as a fertiliser and in horticulture and landscaping. Its land application has a long history, although the recent environmental concerns are increasing scrutiny of this type of disposal. Crop production was investigated, in terms of the location of the activity, nutrient releases from SMC and nutrient soil level – particularly P and N release and concentration, and its effects on various crops; namely tomatoes, lettuce, potatoes and wheat. In addition to these, they consider other applications that have not been so successful. Vermiculture had only a limited use of SMC, anaerobic digestion was not possible due to technological problems and its reuse within the mushroom industry did not meet the required hygiene standards. Moreover, pelleting SMC for fuel was also attempted but was not considered viable – this will be re-evaluated herein.

Maintaining the agricultural context, SMC has also been explored for use with animals. Fazaeli and Masoodi (2006) considered wheat straw-based SMC as a ruminant feed for sheep, investigating its nutritional value. The casing layer was sun-dried and when contained in fodder, up to 20 % was found not to influence the digestibility of dry and organic matter. More than 30 %, however, did affect digestion. Another use was examined by Beattie, *et al.* (2001), who found that SMC could be utilised to beneficial effect through providing a source of environmental enrichment in intensive pig farms, by making it available on a rack above the pigs who can 'nose' and release it. The advantages, compared to the two other cases (no SMC and an empty rack), were that there were fewer instances of aggression, such as tail-biting, and there was less feeding behaviour. They concluded that the presence of a rooting substrate, such as SMC, leads to rooting behaviour not being redirected towards other pigs, thus reducing injuries and maintaining high welfare standards. This would still require disposal after its use.

2.4.3.3 Industrial Uses

There are also a number of industrial uses, as suggested by Rinker (2002); these range from processes for enzyme extraction to uses as a novel biosorbent. Bioremediation for the purification of air, soil and water has been considered by many; a specific application of this is to treat water contaminated from mining. Stark, *et al.* (1994), for example, have looked at how SMC can be used to treat drainage from coal mines. Using high mine drainage flowrates for prolonged periods (> 15 days) led to unfavourable consequence regarding its effectiveness in lowering its redox potential and reducing Fe and Mn outlet concentrations. Although the results for this flowrate are comparable to those for peat, when the flowrate is reduced, the properties of the compost were re-established and iron retention increased. Hammack and Edenborn (1992) examined the removal of nickel from mine waters using acid-washed mushroom compost and Groudev, *et al.* (2004) later conducted a similar study to treat acid drainage from a uranium mine.

Other bioremediation applications using SMC have also been studied; Lau, *et al.* (2003), for example, found that it could successfully immobilise laccase and manganese peroxidase at specific temperatures, where the complete degradative removal of specific PAHs (polycyclic aromatic hydrocarbons), such as naphthalene, phenanthrene, benzo[*a*]pyrene and benzo[*g,h,i*]perylene, from contaminated soils could then be achieved under specialised conditions – 2 days of shaking at 80 °C with 5 % SMC addition. Jordan, *et al.* (2008b) used SMC to aid the re-vegetation of metalliferous (Pb-Zn) tailings, with the aim of enhancing the physical and chemical properties of the pyritic material deposited in an unlined site. Through applying the SMC at various rates to the deposits, the structure of the tailings was improved and nutrients were provided for plant growth – specifically the *Lolium perenne* (perennial ryegrass) sown. Whilst the metal concentrations were found to have been reduced, the deposits could not sustain vegetative cover.

Law, *et al.* (2003) considered the use of SMC from oyster mushroom cultivation (*Pleurotus pulmonarius*) for removing biocide PCP (pentachlorophenol) from water. The removal capacity peaked at 15.5 mg of PCP for 1 g of SMC by biodegradation. Although the SMC was found to contain a PCP-degradative bacterium, it was thought that immobilised ligninolytic enzymes caused most of the biodegradation, through dechlorination, methylation, carboxylation and ring cleavage. The sorption kinetics of PCP removal by SMC was explained by the Freundlich monolayer model. More recently, Chiu, *et al.* (2009) investigated how SMC, also from oyster mushroom cultivation, could aid the removal of petroleum oil from industrial soils. Soil samples contaminated with petroleum hydrocarbons, oil, grease and metals (Cu, Pb and Zn) saw sufficient reductions in these contaminants with the application of small amounts of SMC, through biostimulation, biodegrdation and bioaugmentation. In relatively short time-periods, SMC was able to degrade the fossil fuel contaminants and organopollutants, as well as reduce soil toxicity.

Ball and Jackson (1995) found that physically and/or chemically treated SMC can be used for extracting and recovering lignocellulose-degrading enzymes, which was also true of blended compost extracts; active enzymes were recovered most effectively by blending the SMC in distilled water. This is thought to be useful for upgrading grass lignocelluloses to animal feed. Singh, *et al.* (2003) also investigated the extraction of enzymes from SMC. The use of SMC as a novel biosorbent for adsorbing heavy metals, such as Cd, Pb and Cr from solutions was recently examined by Chen, *et al.* (2005). It was discovered that three key types of functional groups were contained in the biomass: phenolic, phosphoryl and carboxyl groups; these species have the ability to bioadsorb heavy metals, at the levels shown in Table 2.14 and increased with acid pH values.

HEAVY METAL	MAXIMUM UPTAKE OF HEAVY METAL (mg/g)
Cd	833.33
Cr	44.44
Pb	1000.00

Table 2.14: Table of the maximum uptake levels of heavy metals using SMC as a novel biosorbent. Source: Chen, *et al.* (2005)

2.4.3.4 The Diversion of Spent Mushroom Compost from Landfill

Vast amounts of SMC are produced every year, due to increasing demand for mushroom supplies and the ever more commercial nature of operations; despite the many potential uses of this waste product, the increasing amounts that are produced is the most significant barrier to future developments of this industry. The disposal of SMC is becoming increasingly problematic and is a severely limiting factor to the future growth and expansion of this industry (McCahey, *et al.*, 2003); as Williams, *et al.* (2001a, p227-228) state, "the success of the mushroom industry is facing a growing problem . . . (and) further growth of the mushroom industry is not permitted without evidence of a secured SMC waste management solution." There is also legislation to minimise and avoid the disposal of SMC in landfill sites and as implied by the statement above, it is not a sound 'waste management solution'.

This, coupled with the barriers described above, mean that other means of disposal need to be used to maintain the development of the industry and to avoid environmental damage; the possible use of this substance as a fuel, in addition to its other potential uses considered previously, means that disposal in landfill sites would be minimised and hopefully at some point become completely unnecessary. The industrial use of pelletised SMC for energy recovery could therefore make use of any excess compost that is not required for the other agricultural or industrial uses. By making use of this waste and not sending it to landfill or using other environmentally-degrading disposal systems, it is removing the most significant barrier to the further development of the mushroom growing industry, providing a sustainable waste management solution; thus research and developments in this area are clearly important. Using SMC for whatever purpose ensures that there is certainly less or even limited amounts going to landfill.

2.4.3.5 Comparing the Costs

The costs of using or disposing of the SMC vary somewhat; as economics is always the most influential factor in any decision-making process, the price of using SMC needs to be comparable, if not cheaper than disposal in landfill. The cost of landfill is thought to be in the region of £5/t, compared to combustion in a bubbling fluidised-bed, which is around £6.80/t (Williams, *et al.*, 2001a; McCahey, *et al.*, 2003). Disposal, as seen, is often the most economically-viable option though not the most environmental; combustion, however, is likely to become more comparable with disposal, primarily due to vast and continuous increases to landfill tax to encourage more responsible waste management. With increasingly stringent legislation, it is also becoming more difficult to make use of landfill sites.

2.5 COAL: MINES, LAGOONS AND TAILINGS

Coal is widely used for energy generation, although mining leads to the formation of waste – coal tailings. Coal formation and composition are briefly considered, along with the locations of UK mines, which is also where coal tailings, in vast amount, are generally deposited. The composition, properties and potential uses of this waste are then evaluated.

2.5.1 Coal: Formation and Composition

2.5.1.1 Formation, Classification and Typical Coal Compositions

Coal forms from decomposed organic matter that has experienced prolonged burial. It occurs via a two-step process: biochemical decomposition and then coalification. Biochemical decay and decomposition occur after the dead organic matter has accumulated *in situ* under anaerobic conditions, where the bacteria and fungi present transform the material as the water-soluble components decompose; after this, only the more resistant constituents remain. Following the completion of this first stage, the dead, terrestrial woody plant material has become enriched carbon or peat, whose thickness slowly increases (Ristinen and Kraushaar, 1999). As further anoxic decay occurs (maturation or coalification) and the deposits become increasingly buried, chemical and physical changes (humification) occur due to increasing temperature and pressure (Damberger, *et al.*, 1984). The materials become compressed, yielding gases as moisture, and volatiles, such CO_2 and CH_4, are forced out. This process is where peat is converted to coal. Coal has generally been forming since the Upper Palaeozoic, about 250 Ma ago, in the geological period known as the Carboniferous. There were, however, two major phases of coal formation: Carboniferous (the early Triassic period of 200 Ma) and Jurassic (early Tertiary of 50 Ma). The climatic conditions during these were moist and cool, in fact, quite similar to today; all coal in the UK is Carboniferous. Coal was formed in specific geographical locations, mainly widespread deltaic environments that extended into the shallow seas and coastal swamps, and were often covered by large Coal Measure forests. Rapid subsidence in these environments facilitated accumulations of thick organic sediments.

There are different stages in the formation of coal, referred to as 'ranks' – the degree of coalification. As changes occur gradually, the boundaries between these are somewhat arbitrary (Damberger, *et al.*, 1984). Humic coals originate from peat and there are different forms depending on their age and thus their development. The elemental composition, and therefore the chemical and physical properties, vary with rank and depend on the length and depth of burial, geographic location and the composition of the buried material. The main constituents are C, H and O along with small amounts of S and N; there are also varying amounts of volatiles, inorganic mineral matter and a range of trace elements.

Coal is classified into four ranks (Table 2.15); this scheme encompasses chemical composition, including carbon, moisture and ash content, as well as physical characteristics, such as colour, density and presence of woody material. The ASTM (American Society for Testing and Materials) further subcategorise coals depending on the CV and fixed carbon; coals with a fixed carbon content of more than 69 % are categorized according to this, despite their CV, and when fixed carbon is less than 69 %, coals are classified according to the CV, regardless of carbon content. Peat, the precursor to lignite, is not classed as a coal; its CV is lower than lignite and it also has high proportions of moisture. As it is a precursor to coal, it does have some energy value, although it has not been allowed to coalify; this substance forms the casing layer for mushroom compost. Over time, peat gradually develops into lignite, becoming darker as it matures further into bituminous and anthracite coals.

ASTM CLASS	ASTM GROUP	CV (MJ/kg)	%wt FIXED CARBON
Lignite	lignite B	< 14.6	< 69%
	lignite A	14.6 – 19.3	< 69%
Sub-bituminous	sub-bituminous C	19.3 – 22.1	< 69%
	sub-bituminous B	22.1 – 24.4	< 69%
	sub-bituminous A	24.4 – 26.7	< 69%
Bituminous	high volatile C	26.7 – 30.2	< 69%
	high volatile B	30.2 – 32.5	< 69%
	high volatile A	> 32.5	< 69%
	medium volatile	> 32.5	69 – 78%
	low volatile	> 32.5	78 – 86%
Anthracite	semi-anthracite	> 32.5	86 – 92%
	anthracite	> 32.5	92 – 98%
	meta-anthracite	> 32.5	> 98%

Table 2.15: Table identifying coal classes and subcategories.
Source of ASTM classification data: Damberger, *et al.* (1984)

2.5.1.2 Locations of UK Coals

The amount of coal resources are more readily determined than for other fossil fuels, like oil or gas, because it is usually found near the surface. Much coal remains and is distributed across the globe, although not in a uniform manner. Of the 1.2 x 10^{13} tonnes thought to be contained within reserves, most is concentrated in the former Soviet Union (56 % of world total). Western Europe (including the UK) accounts for just 5 % (Dostrovsky, 1988). The distribution of coal in the UK is uneven and since the industrial revolution, mining has taken place in many locations (Figure 2.18a).

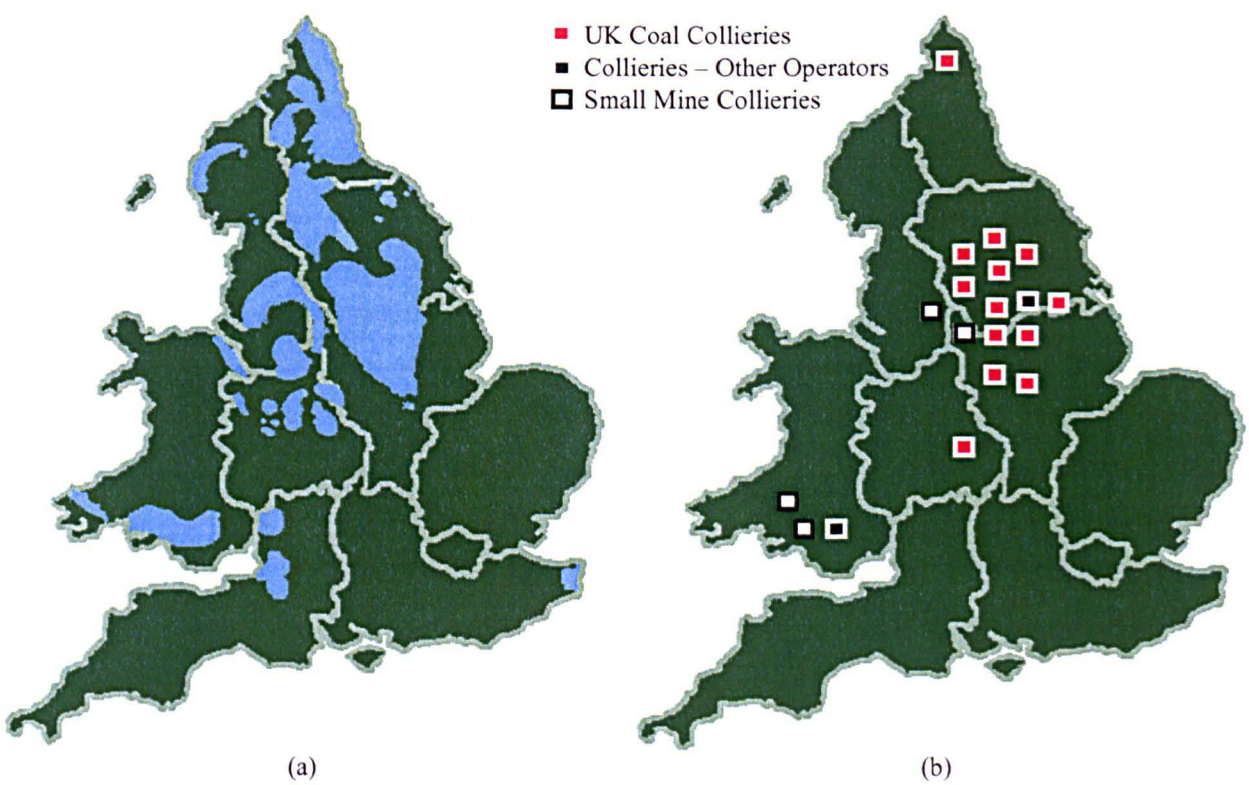


Figure 2.18: The locations of (a) areas affected by coal mining, and (b) current coal mines in England and Wales.
Data Sources: The Coal Authority (n.d.) and IMC Group Consulting Limited (n.d.)

Mining is still of great importance today, with 20.5 million tonnes mined throughout the UK in 2005-2006 (The Coal Authority, n.d.). The locations of operating mines are shown in Figure 2.18b; coal, such as that from these locations, produces almost half of the national energy. Even though there is still much coal left in the UK, a significant proportion has already been utilised and of the remaining coal, not all is economic to mine. As the amount of available coal decreases, these sites may become feasible for coal recovery in the future. Some of this coal is located offshore in the North Sea and it is claimed these areas can continue to provide energy after oil and gas reserves are depleted (The Coal Authority, n.d.).

2.5.2 Coal Mining and Lagoons

2.5.2.1 Coal Mining

Mining coal has been taking place for hundreds of years, utilising various techniques and technologies. Exploratory drilling is initially necessary to acquire core samples for analysis and determine the quantity of coal present at a specific location; this is followed by mining if sufficient reserves are discovered (Speight, 1994). Offshore exploration is now becoming more common and thus the equipment needed in these operations necessitate significant modification to be practical in these extreme environments. There are three primary ways of mining coal: underground, surface and auger mining (Grainger and Gibson, 1981; Speight, 1994; IEA, 1985). The main environmental impacts and considerations associated with coal mining have been outlined by Speight (1994), but are beyond the scope of this research.

2.5.2.2 The Origins of Lagoons and Lagoon Management

These surface and deep mining operations produce coal as well as a number of solid wastes; these wastes include rock and soil, overburden (the extracted overlying strata), coal fines and other refuse, such as coal impurities (Edgar, 1983). Coal preparation involves crushing, screening and washing the ore to remove coal from such contaminants; the undesirable substances (pyrite, calcium carbonate, iron and fine coal of less than 0.6 mm) are known as coal tailings, coal slurry or fines. Lagoons are formed when the coal is separated from these and the materials are released to specific basins, where they collect and form a lagoon (Mathis and Middleton, 1999). These lagoons may be located in the vicinity of current coal mining operations or the mine itself may have been filled with coal tailings once operations have ceased.

Coal tailings contain the inorganic contaminants of the coal and vast quantities of water; before the mixture is placed in lagoons, it may be thickened, through dewatering to 35 % solids (Radloff, *et al.*, 2004). The tailings are left in these lagoons, exposed to the atmosphere; they dry at the surface and drain during warmer, drier weather, but become wetter again when precipitation occurs. In some cases, spoil heaps or lagoons are planted to aid stability and lessen visual intrusion (UK COAL, n.d.). Taylor (1975) discusses the mineralogical and mechanical interrelationships of these; once the coal tailings are buried, the processes of physical breakdown and chemical weathering halt. Thus the mineralogy of the surface tailings may be distinctly different from those at depth. The presence of coal controls the tailings' moisture, shear strength, bulk density and plasticity, although clay minerals also influence the latter two.

Lagoon management is vitally important, as there have been many incidents related to the mismanagement of these sites. The Aberfan disaster, for instance on the 21st October 1966, killed 114 people and initiated both legislation and research into various aspects of coal tailing lagoons (South Wales Police, n.d.). This has in turn led to the implementation of more stringent management and control practices. Lagoons must be designed and constructed in a specific way and awareness of the material properties, such as the presence of coal, to predict its behaviour is vital (Taylor, 1975). Unfortunately, these regulations have not made lagoons completely safe; a recent incident in the Peak District, caused by a dam burst from another slurry lagoon, demonstrates this clearly. It therefore seems of great importance that these sites are managed properly. To eliminate the risks associated with coal tailings and lagoons, the material could be entirely removed in a safe manner to avoid similar disasters in the future. Thompson (1982) identifies many possible solutions to the problems posed by coal tailing disposal; short-term solutions include the re-use of material in the construction industry and the longer-term solutions are the reclamation and restoration of land. Thompson (1982) also suggests that it may be possible to reduce the size of lagoons and perhaps even eliminate the need for them altogether. Through sufficient dewatering of the tailings, lagoon size can be limited. This has not been used to great effect, since the moisture after thickening is still often high, as previously stated. Other uses for this are thus required.

2.5.2.3 Locations of Mines and Lagoons in the UK

Due to their nature of formation, coal tailing lagoons are located within close proximity to mines. There are 7 deep mines in operation located in central and northern England, six of which are licensed to UK COAL, the largest coal producer for energy needs (Figure 2.19). The other deep mine is situated in mid-Glamorgan, licensed to Goitre Tower Colliery Ltd. In addition to the two operating surface mines licensed to UK COAL, there are another 33 situated around the UK (Figure 2.20).

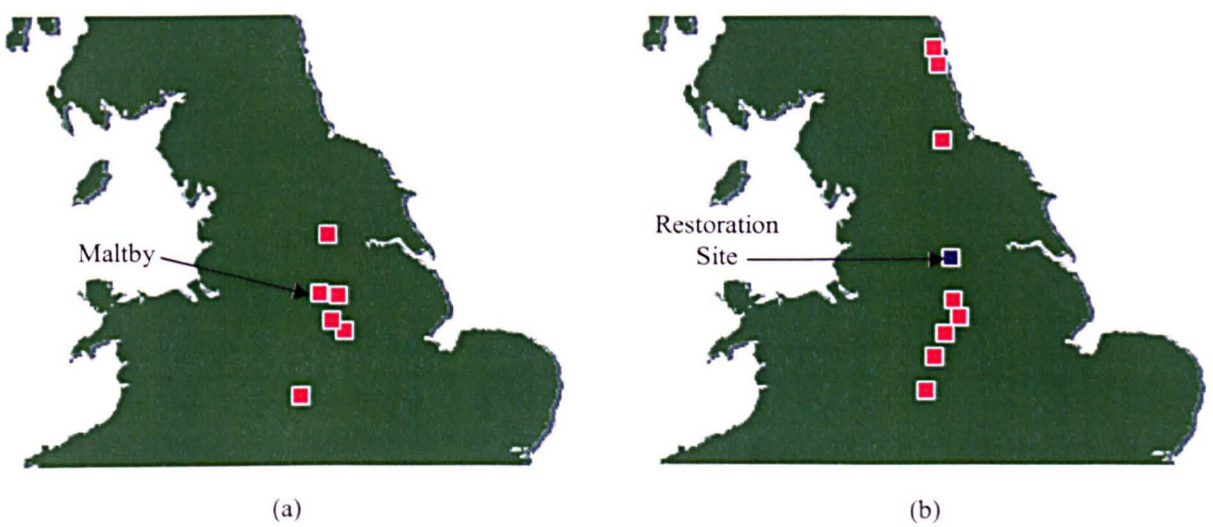


Figure 2.19: Locations of UK COAL (a) deep mines, and (b) surface mines; not all of these are in operation. Source: UK COAL (n.d.)

The colliery operated at Maltby, near Rotherham in Yorkshire, identified on Figure 2.19a, is run by UK COAL and is where the coal tailings for this investigation was sourced. Mining at this location has been

carried out for 100 years and produces very high quality coals for a range of purposes, including energy generation (UK COAL, n.d.). The lagoons for this site and the others are located near to these mines. Thompson (1982) reported that much of the land surrounding collieries are already used to store waste slurries and the continuation of mining activities will therefore increase this problem in the future.

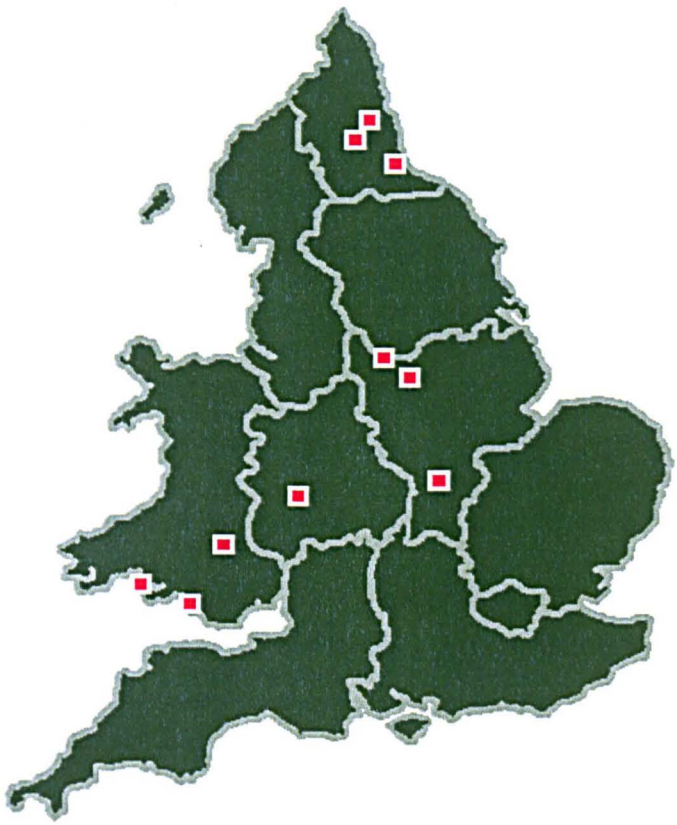


Figure 2.20: Locations of surface mines. At some sites, there are several mines.
Source: DTI (2007)

2.5.3 Coal Tailings

Coal tailings are defined as the fine waste materials (<2 mm) from coal washing and processing, and therefore usually have a high moisture content; it is often referred to as coal tailings, coal slurry, coal waste, coal fines or discard (Radloff, *et al.*, 2004). Found in the above-described lagoons, they are often thickened before being deposited, either through additives or dewatering to some degree.

2.5.3.1 Quantity, Composition and Properties of Coal Tailings

There are many active mines within the UK which produce coal and the amount of coal tailings generated at these sites is usually approximately 10 % of the run-of-mine production (Radloff, *et al.*, 2004). Coal tailings are often thought to be more complex than the coal itself, due to the variability in composition and characteristics (Smoot and Smith, 1985). The composition and properties of various coal tailing samples have been determined in previous research, summarised in Table 2.16. These factors will be analysed for the samples used in this investigation and the results can subsequently be compared to those below.

REFERENCE	MOISTURE (%)	ASH (%)	MEAN PARTICLE SIZE (μm)	CV (MJ/kg)
Radloff, *et al.* (2004)	30	25-40	-	16-22
Sabah, *et al.* (2004)	-	69.7	11.93 μm	-
Franks, *et al.* (2005) – sample 1	-	-	0.4 μm	-
Franks, *et al.* (2005) – sample 2	-	-	10 μm	-
Noble and Dobrovin-Pennington (2005)	32.7	-	-	-
Sis, *et al.* (2004)	-	46.1	-	-

Table 2.16: Table of some of the constituents and characteristics of various coal tailing samples.

As water is usually added, deposits have a high moisture content and thus drying will be required before physical or chemical processing can occur. The ash content is also quite high. If this is mixed with SMC, which also contains significant amounts of ash, the overall ash content of the fuel pellets will be high and may subsequently cause problems. The mean particle size varies greatly between samples, depending on the degree of processing before and after deposition. As the quality of coal is superior to that of the coal tailings, the CV is thus also considerably lower – comparable to the lower rank coals.

2.5.3.2 Potential Uses of Coal Tailings

Coal tailings are rarely used and thus much of the slurries produced through coal mining operations remain in their lagoons. There are, however, a few potential uses of this waste, which are considered here. Relating coal tailings to mushroom production, Noble and Dobrovin-Pennington (2005) studied how it can be used to replace some of the peat in the casing layer that is added to the compost substrate. The initial casing layer used consisted of peat and sugar beet lime; for the tests, 25 % was substituted with a range of substances. Fine coal tailing particles were added to the mixture and it was found that although water retention decreased, the mushroom yield and their heavy metal content were not affected. Coconut fibres, composted bark fines, brown surface peat and black peat were also used; brown peat resulted in an increase in marketable produce, while black peat increased the dry matter in the mushrooms. They concluded that the substitution of this waste is both economically and environmentally advantageous.

Coal tailings and the lagoons in which they are found have been investigated for a variety of purposes within a wide range of scientific research fields (Taylor, 1975). Thompson (1982) suggests it can be re-used for aggregates or the production of concrete construction blocks. Additionally, it is stated that whilst the re-use of coal tailings may be uneconomical at present and perhaps technically unfeasible, this may need to be re-evaluated in the future; this is the focus of this research.

Others have investigated the use of coal tailings as a fuel, once some processing, such as briquetting, has been undertaken; this is in the same context as for this investigation, where coal tailings will be combined with SMC to produce fuel pellets to act as both a binder and a secondary fuel. Radloff, *et al.* (2004) considered the processes involved in turning 70,000 t/a of coal tailings – the waste material from the Wallerawang colliery – into fuel for a power station; they claim that this is the greatest potential use of

this waste and report that it can be combusted with coarse waste from the coal mining industry. Additionally, Tiwari, *et al.* (2004) considered the energy potential of coal slurry, referred to as 'coal-water slurry' (CWS), as an alternative to fuel oils. Through using two anionic additives, high coal loadings and concentrations could be achieved, which also had an appropriate particle size distribution and viscosity. The liquid suspension could be stored for around three weeks. Chugh and Patwardhan (2004) contemplated the economic and technical viability of generating mine-mouth power from processed CWS; the process was found to be feasible on both counts. Through dewatering and capturing the solids at 99.5 % efficiency, the subsequently obtained fuel was combusted in a bench-scale fluidised-bed. Even with high moisture contents (up to 51 %), the combustion efficiency achieved was acceptable and NOx, SOx and mercury emissions were satisfactory. CO release was high, but could be reduced by employing an industrial burner with a hotter cyclone and increased residence times.

Another context within which coal tailing lagoons have been examined is ecological restoration. It has been found that the biodiversity in reclaimed wetlands can be increased if the conditions, mainly the dominant vegetation species, are manipulated (Mathis and Middleton, 1999). Despite these varied uses, the vast majority of the coal tailings are still found within the lagoons where they were deposited and not necessarily managed in an ecological manner. Although Thompson (1982) advocates that much research into the use of coal tailings is required, there does not seem to be much improvement in the situation since then, thus further investigations are clearly necessary.

2.5.3.3 The Clean-Up of Contaminated Land

Coal mines and tailing lagoons are clearly not natural features; the impact they have had is primarily detrimental to the environment, considering the disturbances and disruption both to the surrounding wildlife and their habitat through the removal of soil and vegetation. Moreover, these have had devastating impacts on us, considering the Aberfan disaster and the loss of our habitat. Even though the material dumped in these lagoons is fairly natural, the landscape surface will have changed dramatically (topographical alterations) and the nearby watercourses may also be severely affected.

Additionally, the weathering and/or oxidation of minerals and other species in the newly exposed surface can cause further problems (Speight, 1994). It can therefore be seen that the removal of coal tailings will be beneficial. Complete removal from the environment will need to occur for this, which will need to be disposed of elsewhere; the tailings that have been removed could therefore be used as a fuel, not necessitating further disposal. The contaminated land can be cleaned and restored to its natural state; this is not an easy process and, in fact, a great deal of complex restoration and management strategies needs to be considered. If the reclamation of this land and its subsequent restoration are successful, the area can be returned to something like it once was; it is not to be expected that a full recovery of the land will take place but the habitat and its aquatic and terrestrial wildlife can return to at least a semi-natural state.

2.6 SUMMARY AND CONCLUSIONS

2.6.1 Summary of Topics

Renewable energy and its use are vast topics, within which biomass is the most widely used and perhaps most diverse source. It already plays a significant role in this sector and thus further research into this area is critical to counter the environmental effects of our current use of non-sustainable energy sources. Many types of biomass were investigated herein within the two main categories, wastes or by-products and energy crops, both of which have been further subcategorised depending on the source and/or nature of the fuel. Thermochemical and biochemical treatments are key processes by which these are used, which will be considered in the subsequent chapter. The properties and composition of various biomass fuels were compared, containing a discussion of energy efficiency and recovery. Furthermore, the economic and environmental costs of their production and use were considered. There is much legislation governing the use of energy resources. A number of highly-influential policies have been devised to regulate and address the issues posed to our health and environment. Relevant legislation has been outlined concerning waste and energy generation, such as WID. The use of these resources must conform to such legislation as these preside over the use of such wastes as renewable fuels.

This chapter also investigated SMC. After mushroom cultivation, it is removed from farms and disposed of in environmentally-degrading locations. While there are agricultural and industrial uses, it has been documented that this expanding industry provides an excess that could hence be used for energy recovery. Its use as an energy resource has been previously investigated, although not thoroughly, revealing the necessity for further research in this area. The resources available have been found to be quite large, not only within the UK, thus many countries could utilise this fuel. UK sites where SMC is produced were identified, including the source for this investigation. Although the composition and properties of SMC have been found to not be ideal, processing can make this substance more suitable for thermal treatments. The cost of disposing of SMC in landfill sites has previously been compared to its combustion in a bubbling fluidised-bed. From this review, the use of SMC as a biofuel is deemed necessary; not only to divert it from landfill and avoid the associated environmental effects, but also to combat the unsustainable use of non-renewable energy and mitigate climate change issues, which will improve the economics of its use. A further advantage is that it will ensure the continued development of this industry.

Coal formation was considered; it is intensively mined and thus consumed rapidly, particularly as demand increases yet resources dwindle. The locations of UK coals were identified, and mining and processing in these areas has lead to the formation of coal tailing lagoons, the discarded materials separated from coal. Coal tailing generation is thought to be approximately 10 % of overall run-of-mine production. The management of these locations is vital to ensure their safety, as accidents have previously occurred. Details of how removing coal tailings from lagoons will aid the clean-up of contaminated land were provided. The composition of coal tailing samples has been reported and varies with location; as with the composition and properties of the SMC, these data can also be compared to the experimental results

herein. There are already uses for this waste, including its inclusion in the casing layer for mushroom compost, although these are not extensive; there are also papers available detailing its utilisation as a fuel.

2.6.2 Defining an Opening for Further Research

A number of key topics in this area have been identified and investigated; subsequently, the main conclusions drawn from these were summarised above. In the introduction to this report, a research topic was outlined, and through a comprehensive literature search and review of the information, a definitive area within this field has been identified that warrants further investigation. Whilst energy is vital for our existence, our need for it could eventually cause the devastation of our planet; the increasing use of untenable resources has already led to a range of extensive environmental problems. Although there are a variety of environmentally-sound sources available in the form of renewables, just a few percent of our energy requirements are currently met by these. As fossil fuels start to run out and environmental issues develop further, renewable sources will need to be employed on a larger scale as soon as practicable to avert or at least mitigate the impending environmental and energy crises. Biomass as a renewable resource for energy generation has over recent years become a primary focus of scientific and engineering investigation, within which the types of resources that have been explored are vast. Although SMC has a variety of potential applications, excess compost is still discarded in environmentally-degrading locations. Its use as a biofuel has not been examined to a satisfactory degree, so that it can be utilised as a fuel on a commercial basis and in an economically-viable manner. Its use for combustion purposes has been investigated by Williams (2001), Williams, *et al.* (2001a) and McCahey, *et al.* (2003), and whilst auxiliary fuels were considered, the combination and pelletisation of this material with coal tailings, which would act as a binder and secondary fuel, has not been explored. The use of coal tailing pellets as a source of energy has however previously been considered and deemed practical (Radloff, *et al.*, 2004).

Consequently, the gap within this research area clearly necessitates further investigation to establish whether SMC and coal tailings are suitable substances for pelletisation. Additionally, it is required to ascertain the optimum pellet qualities and then to discover for which thermal energy recovery process these are appropriate. Furthermore, it is important to determine if this is environmentally sustainable and economically-viable. Through various experimental procedures, it can be discovered if SMC-coal tailing pellets can be used in a sustainable and efficient way, which are the key factors in the value of this research. The properties of these materials are less than ideal, thus processing is required to ensure that pelletisation and thermal treatment are favourable; it should be emphasized, however, that substances with apparently similar issues are commercially used as fuels. Moreover, there are other aspects to be taken into consideration; the environmental impacts of the use of these wastes and the economics are further drivers. Legislation may also impact the viability of this, such as the stringent policies concerning the use of non-renewable fuels and increasing landfill tax, which would encourage the investigation of alternative and more responsible waste management solutions. The results of this research concerning both wastes need to be auspicious and are thus vital in the viability of employing these biofuel pellets.

3

THEORY OF THERMAL TREATMENT TECHNOLOGIES AND REVIEW OF CLEAN-UP SYSTEMS

3.1 INTRODUCTION

This first theoretical chapter examines energy conversions for fuels, which can be chemical, physical or biological in origin. Here, they are categorised into thermochemical and biochemical processes, focusing mainly on the various thermochemical treatment techniques (combustion, gasification and pyrolysis), the emissions produced and the associated clean-up technologies employed. The factors affecting whether thermal or biological treatment is required are the cost, availability of the technology or materials and the form of energy required, which are dependent on the properties and quantities of fuel (Wereko-Brobby and Hagen, 1996; McKendry, 2002b). The conversion techniques explored here are related to heat and power generation and the creation of fuels. Although biomass can be used for conversion to chemical feedstocks, these are not covered (McKendry, 2002b).

The emissions produced and the clean-up technologies employed when a fuel is used in one of the above processes are examined; pollutants are formed in many phases, mainly gaseous or particulate, and both are considered herein. The formation, effects and strategies used for the removal of key pollutants are discussed. As the substances used in this investigation are coal tailings and SMC, the final focus of this chapter will be on the primary pollutants produced when they are utilised.

3.2 THERMOCHEMICAL TREATMENTS

Thermochemical processes use heat and/or chemical reactions for upgrading or using a fuel, or converting a substance such as biomass to a fuel with a greater energy content; the main three thermochemical treatments are combustion, gasification and pyrolysis, each which uses progressively less air/oxygen within the system. Figure 3.1 outlines these key processes and the resultant products. This section examines the processes identified in this chart, primarily with reference to biomass.

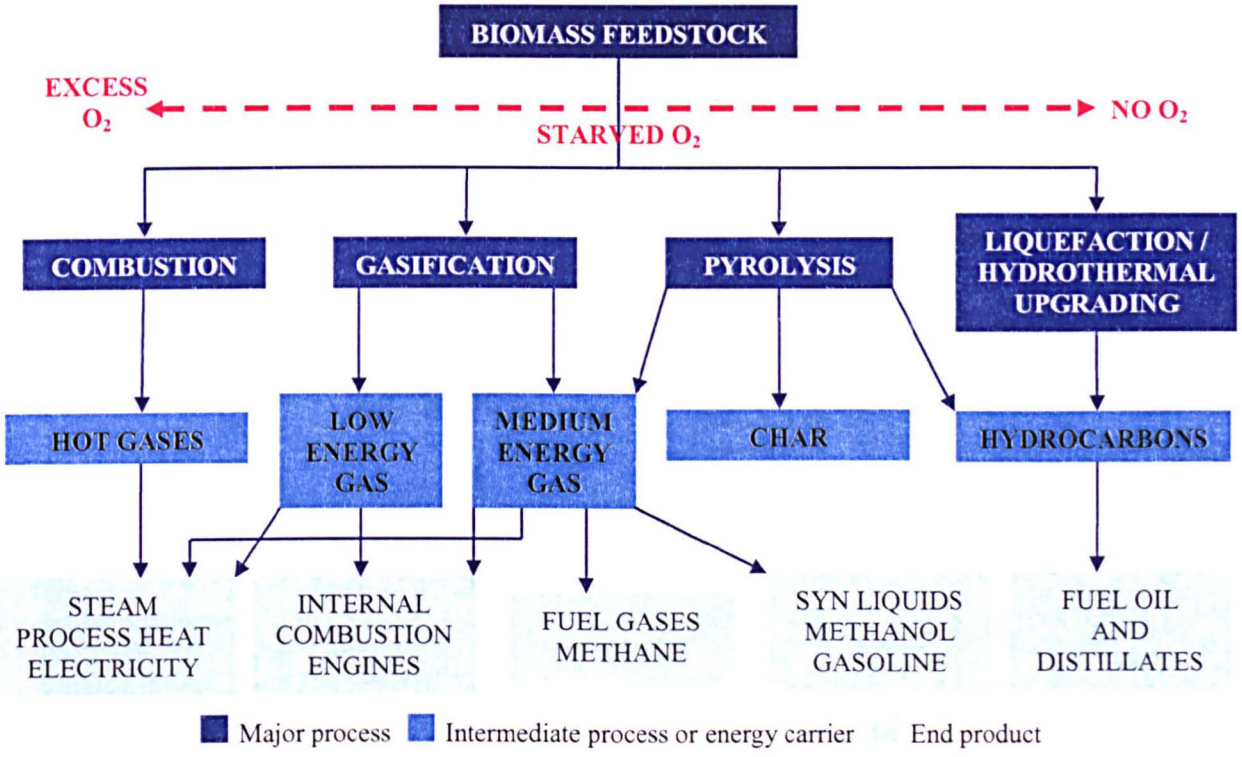


Figure 3.1: Flow diagram of the processes and products of thermochemical treatments.
Source: Adapted from McKendry (2002b)

3.2.1 Combustion

3.2.1.1 Direct Combustion and Co-Combustion

The direct combustion of a fuel, such as biomass, or co-combustion, for example biomass and coal, in air is the simplest way of utilising a material to produce energy and is thus a well-established and extensively employed technology (Bridgewater, *et al.*, 2002). The combustion of fuel results in the generation of hot gases at 800-1000 °C for the production of heat and/or power (Figure 3.1); this process does not, however, create a fuel that can be exploited further (McKendry, 2002b). By combusting raw fuel and not using any pre-processing, the efficiency is often significantly less and the materials more difficult to handle (Wereko-Brobby and Hagen, 1996). Co-combustion involves the burning of biomass and another substance; usually this is coal, and occurs in coal-fired power stations (Bridgewater, *et al.*, 2002). This is thought to be advantageous as high conversion efficiencies can be achieved, more so when large systems (100 MWe or more) are used (McKendry, 2002b).

As the analysis of composition for biomass (Section 2.2.3) and SMC (Section 2.4.2) show, fuels are composed of four key constituents: moisture, volatiles, fixed carbon and ash. After the fuel is fed into the reaction chamber, its combustion consists of a variety of stages, each relating to these components, as outlined here and depicted in Figure 3.2. Drying and devolatisation occur in the first stage, where heat is provided to the raw material through: (i) heated primary air injections from below the bed, (ii) through radiative heat transfer from the walls, and (iii) by the hot gaseous combustion products from latter stages. This causes the temperature of the fuel to increase (heat-up zone, Figure 3.2) and the free moisture is driven off at 50-100 °C. As the temperature increases further, the bound moisture is also liberated and the material starts to thermally decompose, or pyrolyse (pyrolysis zone), between 200 °C and 750 °C, whereupon the volatiles are released. These volatiles are composed of hydrocarbons, up to 90 %, and other combustible species, like CO and H_2.

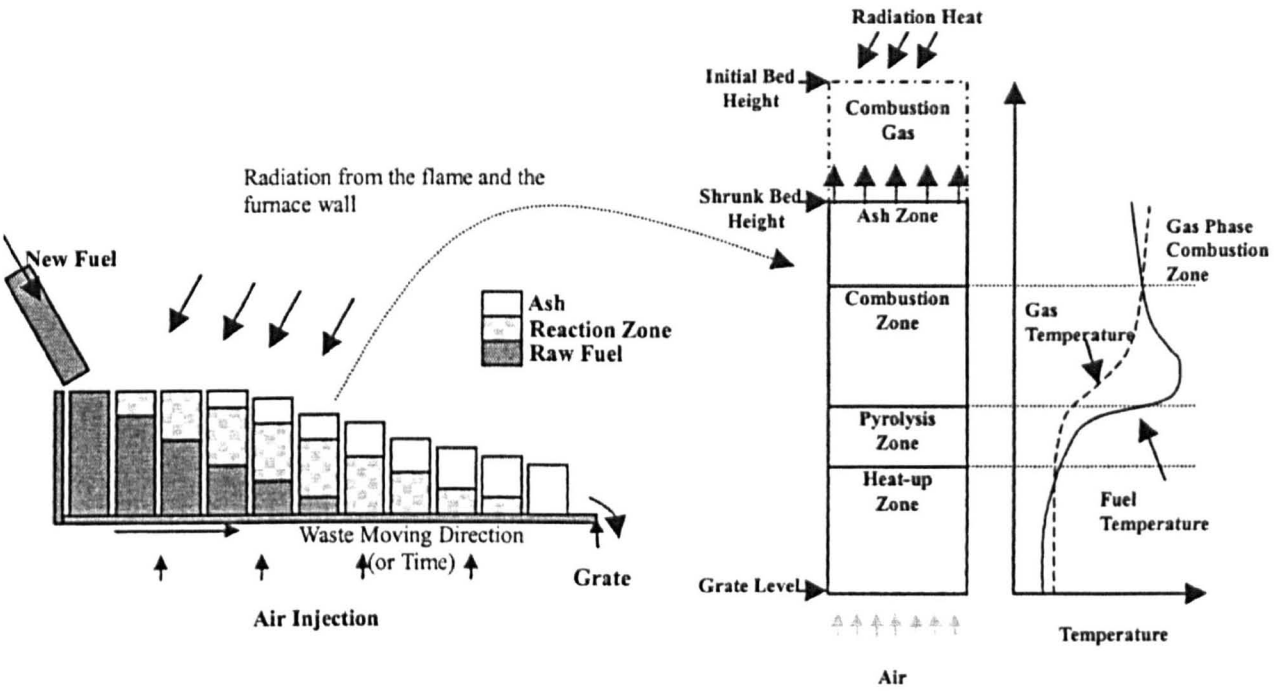


Figure 3.2: Combustion of a solid fuel, in this case, in a bed.
Source: Shin and Choi (2000)

Next, there are two combustion stages, as there are two combustible constituents. The first is the combustion of the released volatile matter (combustion gas) and any soot, which occurs above the bed in the freeboard zone at very high temperatures, in excess of 1000 °C. This is needed along with sufficient residence times and surplus turbulent secondary air to ensure mixing and minimise pollutant formation. This combustion phase occurs very rapidly and it is believed that the volatiles combust through the following reactions (Williams, *et al.*, 2001b):

$$\begin{aligned} \text{volatiles} + O_2 &\rightarrow CO_2 + H_2O \\ CO + \tfrac{1}{2}O_2 &\rightarrow CO_2 \end{aligned} \qquad (3.1)$$

In the second stage, where both moisture and volatiles have been removed, the remaining solid material – carbonaceous char – combusts in the bed (combustion zone); this oxidation occurs at a significantly

slower rate and therefore can take considerably longer than the previous stage, depending on the ratio of volatiles and fixed carbon in the fuel. The following reactions give off heat, which is then utilised for power production (Rezaiyan and Cheremisinoff, 2005):

$$\begin{aligned} C + O_2 &\rightarrow CO_2 \\ C + \tfrac{1}{2}O_2 &\rightarrow CO \\ H_2 + \tfrac{1}{2}O_2 &\rightarrow H_2O \end{aligned} \qquad (3.2)$$

The residue left after the two combustion stages is the ash (ash zone) and any other non-combustible material. For biomass, it is not unusual that the majority of energy is derived from volatile matter, unlike coal, where most energy comes from the combustion of char; due to this, it is vital that any combustion processes make use of these volatiles, as well as the solid substances, to ensure high efficiencies (Ramage and Scurlock, 1996). Combustion therefore needs to be carefully controlled, where the oxygen supply is regulated to increase efficiency and the pollutants, both gaseous and particulate, can be minimised. Although in theory any biomass can be combusted, in practice only biomass with less than 50 % moisture can be burned successfully without pre-drying. If the moisture is too high to make this viable, biological conversions are often employed instead (McKendry, 2002b).

Although biomass combustion is generally well understood, many complex routes that arise have resulted in the computational modelling of particle combustion (Bridgewater, *et al.*, 2002). This is a relatively new research area that is gaining significant attention. Porteiro, *et al.* (2006, p169), for example, have recently modelled the combustion of a single wood particle and densified biomass particles; their validated one-dimensional model incorporates a "novel discretisation scheme and . . . intra-particle combustion processes with extra-particle transport processes". It agrees well with previous data and can predict trends detected in experimentation for pellets of varying size. Combustion processes, regarding biomass or any other material, produce emissions that often cause detrimental effects on the environment and our health, as discussed in detail later in this chapter. Jenkins, *et al.* (1998) investigated the effect of biomass composition on its combustion properties; through examining the formation of pollutants and the initial species present within the feedstock that are the cause of these, they suggest that standard engineering protocols are required to deal with the undesirable consequences of biomass combustion.

3.2.1.2 Combustion after Physical Processing

Modifying the physical properties of fuels is a simple and often cost-effective way of making them more appropriate for use in various types of combustors. Forming pellets from biomass or coal, for instance, is common and they can be used for combustion on a variety of scales, from directly heating domestic buildings to generating power at an industrial level; straw and wood residues are frequently used for this purpose (Holm, *et al.*, 2006). Co-firing of processed biomass with another fuel, such as coal, is known as indirect co-combustion, compared to direct co-combustion discussed above. The purposes of pelletisation and the processes involved are considered subsequently. The drying of biomass is also of particular use, as the CV is highly influenced by moisture and can be appreciably reduced due to the volatilisation of

vast amounts of water (Wereko-Brobby and Hagen, 1996). Improving the efficiency by drying is a way of increasing the energy produced, normally with fairly minimal energy inputs. Other physical processing includes chipping, chopping and grinding (Wereko-Brobby and Hagen, 1996). Each of these aids the use of the product for particular combustors, such as fluidised-beds (discussed in the following chapter) and so each process is tailored individually to suit a specific need, for example the size of the biomass chips. These processes do, however, result in larger energy inputs and thus increased costs.

3.2.2 Gasification

Gasification is where a solid, fairly homogeneous material is subjected to high temperatures to form gaseous fuels by partial oxidation (Figure 3.1); this reaction can take place at a variety of temperatures and pressures, in a range of gasifiers (Ramage and Scurlock, 1996; McKendry, 2002b). The development of such systems has an extended history, particularly for coal, from which much biomass gasification technologies are borrowed (Bridgewater, *et al.*, 2002; Belgiorno, *et al.*, 2003). Biomass gasification forms syngas through partial combustion, whereby combustible solids are converted to combustible gases to preserve their original energy. The key constituents are water vapour, H_2, CO, CO_2, CH_4 and other hydrocarbons, as well as nitrogen, if air is used (Ramage and Scurlock, 1996). There are three main modes of gasification, where the agents used are air, oxygen or steam; there are significant cost increases for each of these. Air ensures the temperatures required are low, decreasing the production costs, but the products have significantly lower CVs, due to their dilution with nitrogen; new technologies, however, mean these fuels can now be used (Wereko-Brobby and Hagen, 1996). The fundamental equations outlining the mechanism for gasification are the complete and partial oxidation of C (McKendry, 2002c):

$$\begin{aligned} C + O_2 &\leftrightarrow CO_2 \ (\Delta H = -406 \text{ MJ/kg mole}) \\ C + \tfrac{1}{2}O_2 &\leftrightarrow CO \ (\Delta H = -268 \text{ MJ/kg mole}) \\ 2CO &\leftrightarrow C + CO_2 \end{aligned} \qquad (3.3)$$

The first and second of these are exothermic oxidation reactions and the third is the endothermic Boudouard reaction (Williams, 1998). The syngas produced from gasification in air generally has a fairly low CV, typically 4-8 MJ/m^3, whereas this can be greatly improved if oxygen is used (8-14 MJ/m^3), and increased even further by utilising steam, to produce a syngas with an energy content of 14-20 MJ/m^3. This process involves four reactions; the first are two endothermic carbon-steam or water-gas reactions (Williams, 1998; McKendry, 2002c; Rezaiyan and Cheremisinoff, 2005):

$$\begin{aligned} C + H_2O &\leftrightarrow CO + H_2 \ (\Delta H = 118 \text{ MJ/kg mole}) \\ C + 2H_2O &\rightarrow CO_2 + 2H_2 \end{aligned} \qquad (3.4)$$

Next is the exothermic water-gas shift reaction, where optimum hydrogen yields are obtained at low temperatures. Lastly, the exothermic hydrogenation or hydro-gasification of C occurs, which is slow except when high pressures are used (McKendry, 2002c):

$$\begin{aligned} CO + H_2O &\rightarrow CO_2 + H_2 \ (\Delta H = -42 \text{ MJ/kg mole}) \\ C + 2H_2 &\rightarrow CH_4 \end{aligned} \qquad (3.5)$$

At high pressure, further exothermic hydrogenation/methanation reactions occur (McKendry, 2002c):

$$CO + 3H_2 \rightarrow CH_4 + H_2O \ (\Delta H = -88 \text{ MJ/kg mole})$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (3.6)$$

In addition to the gasifying agent employed, the temperature and pressure affect the syngas CV and composition (Rezaiyan and Cheremisinoff, 2005). Gasifier efficiencies vary, although they can high (up to 72 %), whilst the CV is often less than 6 MJ/N m^3, particularly with air (McKendry, 2002b). Syngas with a low CV is combusted directly or used as engine fuel, whereas those with greater energy contents are used as feedstocks for further processing (McKendry, 2002c). Gasification and pyrolysis have many advantages over incineration; they produce fewer emissions, are flexible and provide a range of fuel products at high efficiency. The challenges are the cleaning and quality of the syngas. Despite this, another distinct advantage of gasification is that the fuels are often cleaner to use than the biomass itself and the pollutants formed can be removed more easily (Ramage and Scurlock, 1996). Furthermore, gaseous fuels are more versatile in their applications.

Using biomass gasification and gas turbines to produce electricity in a combined cycle – biomass integrated gasification/combined cycle – has a high conversion efficiency. An additional advantage is that the gas is cleaned prior to use, enabling smaller, cheaper cleaning equipment to be installed (McKendry, 2002b). Much work has been carried out to investigate the feasibility of this. de Souza-Santos (1999) examined atmospheric gasification of sugar cane bagasse, coupled with a fluidised-bed heat exchanger and Albertazzi, *et al.* (2005) explored hydrogen production through biomass gasification. Belgiorno, *et al.* (2003) investigated syngas production from MSW gasification; through evaluating the system, the potential uses for the syngas and the current scheme of waste management, they determined the environmental implications of reusing this waste – significant energy recovery and noticeable pollutant reductions. McKendry (2002c) explored biomass gasification technologies in great detail; through an investigation of the basic chemistry, the pre-treatments necessary and the optimum feedstock properties were established, along with the different types of gasifiers. There are two main types (Table 3.1), of which there are several variations depending on the direction of the flow, shown in Figure 3.3 (Wereko-Brobby and Hagen, 1996). There are also other designs, such as moving beds, rotary kilns and cyclone reactors, each with their relative merits concerning the conversion rate, efficiency, capacity, residence times, tar production, complexity of construction, solid-gas contacting and temperature control.

TYPE OF GASIFIER	SUBCATEGORIES
Fixed-Bed	down-draught up-draught cross-draught/cross-flow
Fluidised-Bed	circulating bubbling

Table 3.1: The types and subcategories of different gasifying equipment used for biomass conversions. Source: Wereko-Brobby and Hagen (1996); McKendry (2002c)

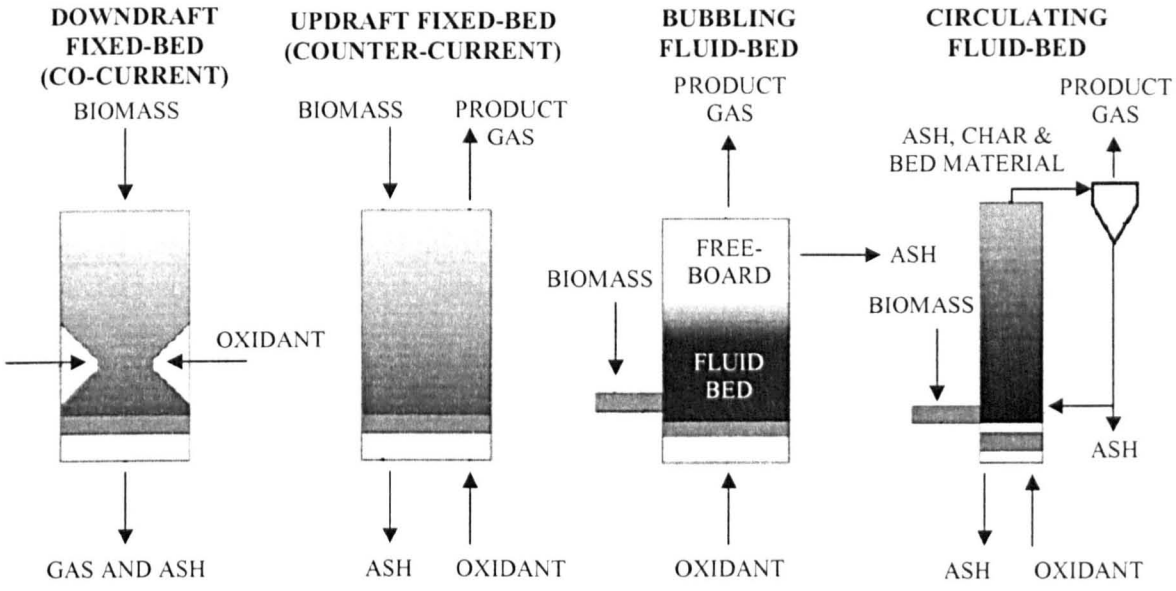


Figure 3.3: The main types of gasifiers, as explained in Table 3.1. The third type of fixed-bed gasifier, the cross-draught gasifier, is not shown.
Source: Bridgewater, *et al.* (2002)

3.2.3 Pyrolysis

Pyrolysis involves the heating of biomass or other materials with a restricted air supply and is a simple technique of enhancing a dry fuel, of small particle size, by thermal degradation (Bridgewater, *et al.*, 2002). Due to this and the absence of air from the system, the products, shown in Figure 3.1, are in the form of condensed gases (up to 80 % yield), pyrolytic or bio-oils (up to 80 % yield), pyroligneous acid and charcoal (up to 35 % yield), all of which can be used as fuels (Wereko-Brobby and Hagen, 1996; McKendry, 2002b). These generally have a low to moderate CV, yet their energy densities are frequently far superior to the original biomass (Horne and Williams, 1996; Bridgewater, *et al.*, 2002). Due to this, there are many applications for these products, including the production of electricity or use in a CHP station; they can also be used as transport fuels and chemical feedstocks (Bridgewater, *et al.*, 2002). Upgrading the resultant oils is often required owing to their poor thermal stability and/or corrosive nature.

There are two main processes by which pyrolysis is achieved – slow or fast pyrolysis; a range of other technologies can also be employed, the conditions of which are summarised and compared in Table 3.2. Conventional (slow) pyrolysis is where biomass is slowly heated to 300-600 °C without air; the volatile matter is eliminated and the energy density of the remaining char is much higher (Ramage and Scurlock, 1996). This is another way of carbonisation, where the char yield is maximised. The second method, fast or flash pyrolysis, uses more sophisticated processes, higher temperatures and a faster heating rate to collect the volatiles driven off and convert more of the substance to these gases, leaving only approximately 10 % as char. Controlling the temperature increase and the final temperature enables the composition of the resultant gas to be manipulated and form bio-oils after rapid quenching (Ramage and Scurlock, 1996; Bridgewater, *et al.*, 2002; McKendry, 2002b). Using short residence times and moderate temperatures (400-550 °C) maximises pyrolytic liquid yields (Horne and Williams, 1996).

PYROLYSIS TECHNOLOGY	RESIDENCE TIME	HEATING RATE	TEMPERATURE (°C)	PRESSURE (bar)	MAIN PRODUCTS
Carbonisation	hours – days	very low	400	1	charcoal
Conventional	10 s – 30 mins	quite low	~600	1	gas, liquid oil and char
Flash – Liquid	<1 s	high	600-650	1	liquid oils
Flash – Gas	<1 s	high	650-700+	1	gas
Ultra	<0.5 s	very high	1000	1	gas
Vacuum	2-30 s	medium	400	<0.1	liquid oils
Hydropyrolysis	<10 s	high	<500	~20	liquid oils
Methanolysis	0.5-1.5 s	high	700-1050	~3	benzene, toluene, etc.

Table 3.2: Comparison of different types of pyrolysis.
Source: Williams (1998); Rezaiyan and Cheremisinoff (2005)

The pyrolysis of biomass, although highly complex, is understood to some degree in terms of the reactions undergone by the cellulose and starch components, which often make up a significant proportion of the feed material. Other reactions may include cracking, thermal degradation, repolymerisation and evaporation. Exothermic carbonisation or charring is the first reaction to occur and results in the production of charcoal (Boyles, 1984):

$$[C_6H_{10}O_5]n \rightarrow 6nC + 5nH_2O \tag{3.7}$$

The next reaction is again exothermic, where the pyrolytic oil (assumed to be C_6H_8O) is formed and finally, the syngas is produced, via a water-gas reaction, which is endothermic:

$$\begin{gathered}[C_6H_{10}O_5]n \rightarrow 0.8nC_6H_8O + 1.8nH_2O + 1.2nCO_2 \\ C + H_2O \leftrightarrow CO + H_2\end{gathered} \tag{3.8}$$

These pyrolysis mechanisms have been investigated by Blesa, *et al.* (2001), who explored the pyrolysis and subsequent briquetting of coal-sawdust mixtures, where pyrolysis occurred at 400-600 °C. Bridgewater, *et al.* (2002) also investigated four options for the thermal treatment of biomass to produce electricity; of these, fast pyrolysis was the cheapest, although they did highlight that the costs were indeed very similar between the other options (combustion and atmospheric or pressurised gasification).

3.2.4 Liquefaction and Hydrothermal Upgrading

The three processes described above are the most common thermochemical treatments used for biomass and other fuels; although liquefaction and hydrothermal upgrading are employed less frequently, they can be used to treat biomass and produce bio-oils (McKendry, 2002b). Liquefaction produces liquid hydrocarbons using high pressures and low temperatures, where hydrogen aids the conversion process. Compared to pyrolysis, the wider use of this is limited by the somewhat complex and expensive nature of the operation.

Hydrothermal upgrading is a simple procedure, whereby biomass is converted in wet conditions to partially oxygenated hydrocarbons; this also takes place at high pressures. The products and their uses, from both these processes, were shown in Figure 3.1.

3.3 BIOCHEMICAL PROCESSING: ALTERNATIVES TO THERMAL TREATMENT

There are also two main biochemical treatment methods used to transform biomass into secondary fuels – so-called 'biofuels'. These are fermentation/oil extraction and anaerobic digestion, both of which use microbiological action to convert the feedstock (Wereko-Brobby and Hagen, 1996).

3.3.1 Fermentation and Oil Extraction

Fermentation is the manufacture of alcohol fuels, such as methanol and ethanol, under anaerobic conditions using a biological process (Ramage and Scurlock, 1996). These are often large-scale systems, where biomass is pounded, then biologically treated with enzymes (McKendry, 2002b). Not only are there different processes for producing methanol and ethanol, but they also vary depending on the feedstock used, for example sugar crops (sugar cane or beet), starch crops (maize or wheat) or cellulose (Wereko-Brobby and Hagen, 1996; McKendry, 2002b). The products have a variety of uses; they can be used in internal combustion engines or as a 'gasoline extender' to form gasohol – a combination of gasoline and an alcohol, often ethanol (Ramage and Scurlock, 1996). For ethanol production from sugars, the pre-treatment involves washing, crushing, filtering, concentrating and sterilising the feedstock; the remaining sugar liquid is fermented and ethanol can be distilled (Wereko-Brobby and Hagen, 1996). When ethanol is manufactured from cellulosic or starch-based biomass, additional conversion processes are required, increasing the costs, as these need to be converted to sugars by enzyme-induced hydrolysis and hydrolysis/saccharification respectively (Wereko-Brobby and Hagen, 1996). In addition, these products usually require purification through energy-intensive distilling. The by-products (solid residue) are used as animal fodder. Sugar bagasse is another fuel produced via this mechanism (McKendry, 2002b). Hamelinck, *et al.* (2005) evaluated lignocellulosic biomass as a means of ethanol production using hydrolysis-fermentation technologies; efficiencies of 35 % are usual, although the overall process efficiency can be increased to 68 % if non-fermentable lignin is used to co-generate electricity.

Methanol manufacture is somewhat different, taking place in stages: firstly, a gaseous intermediate from the biomass is formed and secondly, methanol is produced from this (Wereko-Brobby and Hagen, 1996). As above, converting starch or cellulosic biomass necessitates more processing, as they require conversion to sugars by saccharification, for starch, or by hydrolysis for cellulose (Wereko-Brobby and Hagen, 1996). Lignocellulosic biomass conversion is made more complex by the long-chain molecules present (McKendry, 2002b).

Oil and ester extraction to produce vegetable oils and methyl/ethyl esters is performed using solvent removal techniques or mechanical crop pressing (Usta, 2005). The former is more efficient although the latter is significantly simpler – only involving heating the crop and gradually applying pressure to remove 95 % of the oil (Wereko-Brobby and Hagen, 1996). For solvent extraction, highly-refined and advanced technologies are required, employing a chemical solvent, usually hexame. These are used directly as

fuels, usually in diesel compression ignition engines, as Usta (2005) investigated for tobacco seed oil (a by-product of the tobacco industry) and tobacco seed oil methyl ester. It was found that partial substitution of diesel by the ester can occur without alterations to the engine.

3.3.2 Anaerobic Digestion

This biological conversion process uses bacterial decomposition to produce biogas consisting primarily of CH_4 (~60 %) with smaller proportions of CO_2 (~35 %) and yeah (~5 %), a mixture of hydrogen, nitrogen, ammonia, hydrogen sulphide, CO, oxygen, volatile amines and water (Wereko-Brobby and Hagen, 1996). Removing significant proportions of CO_2 can considerably improve the quality (McKendry, 2002b). The initial input into the digester varies, although it often contains plant material, as well as animal and poultry manure; MSW can also undergo this process, which produces a fuel with a CV of 20-25 MJ/m^3. The overall digestion process is where micro-organisms convert the organic matter by breaking down the material into CH_4 in the absence of air in prefabricated digesters. The factors affecting the production rate efficiency are the pH, holding time in the digester and the material loading rate (Wereko-Brobby and Hagen, 1996). Biomass undergoes anaerobic digestion in a variety of stages, which occur concurrently in a digester, of fixed-dome or floating gas design (Wereko-Brobby and Hagen, 1996). The first, hydrolysis, is where large, complex molecules are decomposed by enzyme action to smaller, simpler ones, which pass through the bacterial membrane. The hydrolysis reaction using cellulose to form glucose is:

$$(C_6H_{10}O_5)n + H_2O \rightarrow n(C_6H_{12}O_6) \tag{3.9}$$

The next phase is the acid stage, where acid-forming bacteria produce organic acids and other products from complex fats and proteins. Lactic acid is produced from the glucose formed above by:

$$(C_6H_{12}O_6) \rightarrow CH_3CH(OH)COOH \tag{3.10}$$

The final stage is known as the methane phase, as CH_4 is produced via reactions between hydrogen and CO_2, as well as during the fermentation of acids and alcohols:

$$\begin{gathered} 4H_2 + CO_2 \rightarrow 2H_2O + CH_4 \\ CH_3CH_2OH + CO_2 \rightarrow CH_3COOH + CH_4 \\ CH_3COOH \rightarrow CO_2 + CH_4 \\ CH_3CH_2CH_2COOH + H_2O + CO_2 \rightarrow CH_3COOH + CH_4 \end{gathered} \tag{3.11}$$

Biogas and LFG are both formed by these processes, which are in fact quite similar, although biogas production is more controlled. Conditions in landfills can be manipulated to ensure LFG is produced at a more rapid rate, where such a highly managed environment is also beneficial in terms of safety. As previously stated, biomass with high moisture is better suited to bio-chemical conversion than thermo-chemical operations and the use of anaerobic digestion is therefore ideal for treating certain types of biomass. Biogas can be used directly in spark ignition gas engines, where the efficiency is 10-16 %, or it can be used to generate electricity in gas turbines (McKendry, 2002b).

3.4 FORMATION, EFFECTS AND REMOVAL OF POLLUTANTS

Pollutant emissions, both gaseous and particulate in form, produced from thermochemical treatments can be problematical to the environment and human health. Here, the main gas-phase species and particulate emissions are considered in terms of their formation, effects and removal.

3.4.1 Gaseous Emissions

3.4.1.1 Carbon Monoxide and Carbon Dioxide

CO and CO_2 are two products obtained from the combustion of fuels; both are highly undesirable to release to the atmosphere and form through the progressive oxidation of fuel:

$$CH_4 \rightarrow CH_3 \rightarrow CHO \rightarrow CO \rightarrow CO_2 \qquad (3.12)$$

CO forms on incomplete combustion; the greatest source, however, is not from power stations, but transportation, where conditions are not as highly controlled. Three factors lead to the formation of CO rather than CO_2: (i) lack of O_2 to complete oxidation, (ii) poor fuel-oxidiser mixing or (iii) contact with cool surfaces, which condense and quench the reaction. Not only is CO toxic, but it also aids greenhouse gas formation by reacting with other species to increase atmospheric ozone and methane concentrations, so it is vital that practices are employed to minimise CO formation and/or release. There are four key ways of reducing CO formation; the first three involve modifying the system to eliminate the above three conditions, with the fourth being lean burner engines or catalytic converters with a rhodium (Rh) or platinum (Pt) mesh to aid complete combustion.

Although CO_2 is undesirable, it is not toxic so is preferred to CO. It is formed when combustion goes to completion (Equations 3.2 and 3.12), and C is fully oxidised via the catalysed water-gas phase shift reaction (Equation 3.5 above), compared to CO, where only partial oxidation occurs. CO_2 is a greenhouse gas, the most prominent in the atmosphere, as shown in Table 1.1, and has adverse environmental impacts (Grainger and Gibson, 1981). There are many ways to reduce emissions, classified as combustion technologies or post-combustion capture and storage, where the latter is thought to be more realistic (DTI, 2000). Capture technologies include absorption, cryogenics, adsorption and the use of membranes. Storage locations for the collected gas comprise depleted oil and gas reserves, deep saline reservoirs, unmineable coal beds and oceans.

3.4.1.2 Acid Gases: NOx, SOx and HCl

Acid gases comprise oxides of nitrogen and sulphur, as well as hydrogen chloride, which cause significant problems if they are not removed from the exhaust gas, as they can become dissolved in any condensing water vapour in the atmosphere to form corrosive acids. The term NOx is used to include NO, colourless nitric oxide, and NO_2, brown nitrogen dioxide; nitrous oxide (N_2O) – the greenhouse gas – is not a NOx compound. NO is formed via three mechanisms: fuel NOx, prompt NOx and thermal NOx.

The first is the most common, contributing up to 80 % of total NOx emissions, when the N bound in the fuel is oxidised. The amount of nitrogen in the fuel and the oxygen concentration are the controlling factors, where combustion in rich environments produces significantly lower fuel NOx (Smoot and Smith, 1985). Intermediate compounds, hydrogen cyanide (HCN) and ammonia (NH_3), form before full oxidation occurs:

$$\begin{aligned} HCN &\rightarrow NCO \rightarrow NO \\ NH_3 &\rightarrow NH_2 \rightarrow NH \rightarrow NO \end{aligned} \qquad (3.13)$$

Typically less than 5 % of total NOx comes from prompt formation, where hydrocarbon fragments react with N at the flame front in fuel-rich environments (Smoot and Smith, 1985):

$$CH + N_2 \rightarrow HCN + N \qquad (3.14)$$

The HCN that is subsequently produced can partake in various oxidation reactions:

$$\begin{aligned} HCN + O &\rightarrow NCO + H \\ NCO + O &\rightarrow NO + CO \end{aligned} \qquad \begin{aligned} HCN + O &\rightarrow NH + CO \\ NH + O &\rightarrow NO + H \end{aligned} \qquad (3.15)$$

The Zeldovich mechanism forms thermal NOx when N in the combustion air is oxidised; the combustion of any fuel in air leads to the formation of thermal NOx, up to 25 % of the total, thus combustion in oxygen can eliminate NOx from this source (Smoot and Smith, 1985). Reactions are slow but become increasingly rapid as temperatures rise. These include (Edgar, 1983):

$$\begin{aligned} O^{\cdot} + N_2 &\rightarrow NO + N^{\cdot} \\ N^{\cdot} + O_2 &\rightarrow NO + O^{\cdot} \\ N^{\cdot} + OH &\rightarrow NO + H^{\cdot} \end{aligned} \qquad (3.16)$$

NO_2 is formed via further oxidation of NO, either directly, which is extremely slow, or by other compounds, such as radicals that can be rapid, particularly in cooler regions of the flame:

$$\begin{aligned} NO + \tfrac{1}{2}O_2 &\rightarrow NO_2 \\ RO_2 + NO &\rightarrow RO + NO_2 \\ HO_2 + NO &\rightarrow HO + NO_2 \end{aligned} \qquad (3.17)$$

Although NOx are undesirable, as they are toxic and contribute to environmental problems including acid rain, ozone depletion, the formation of photochemical smog and the enhanced greenhouse effect, combustion is the main source of their emissions (Grainger and Gibson, 1981; Edgar, 1983). Some key conditions necessary for NOx formation have been outlined above; manipulating these can reduce emissions, including using rich combustion environments to reduce fuel NOx or using oxygen instead of air to minimise thermal NOx (Berkowitz, 1979). These are combustion modification techniques and although they are simple, they can be expensive. Another technology in this category is low-NOx burners, which introduce extra air and reduce combustion temperatures, coupled with flue gas recirculation to recycle gases, further reducing the temperature (Berkowitz, 1979; Edgar, 1983). Fuel and air staging can minimise NOx formation or reduce them to nitrogen; common problems associated with these include slagging and fouling (Edgar, 1983; Coal R&D, 1997). Other technologies are classified as

flue gas treatment, although the most effective are also the most expensive. Many focus on the removal of NOx from a non-thermal origin. Selective non-catalytic reduction (SNCR) uses an aqueous NH_3 solution or urea ($CO(NH_2)_2$) injected directly into the flue gases at 900-1000 °C (Edgar, 1983); although this can lead to N_2O production, it can eliminate up to half of NOx emissions, by reducing them to molecular nitrogen (Coal R&D, 1997):

$$\begin{aligned} 4NH_3 + 4NO + O_2 &\rightarrow 4N_2 + 6H_2O \\ 2CO(NH_2)_2 + 4NO + O_2 &\rightarrow 4N_2 + 2CO_2 + 4H_2O \end{aligned} \qquad (3.18)$$

Selective catalytic reduction, SCR, is more efficient, also using an ammonia injection in the flue, at 300-400 °C to achieve very high removal efficiencies, often 80-90 % (Edgar, 1983; Speight, 1994). An oxide of tungsten (W), titanium (Ti) or vanadium (V) in a honeycomb structure is also required to act as a catalyst, increasing costs to £600 per tonne of NOx removed. Both NO and NO_2, however, can be reduced in this way (Coal R&D, 1997):

$$\begin{aligned} 4NO + 4NH_3 + O_2 &\rightarrow 4N_2 + 6H_2O \\ 2NO_2 + 4NH_3 + O_2 &\rightarrow 3N_2 + 6H_2O \end{aligned} \qquad (3.19)$$

SOx, oxides of sulphur, are formed when sulphur in fuels is oxidised during combustion. The first compound to arise, sulphur monoxide (SO), is highly unstable and is thus rapidly oxidised to sulphur dioxide (SO_2); sulphur trioxide (SO_3) then forms using an energy absorber (M):

$$\begin{aligned} SO + O_2 &\rightarrow SO_2 + O \quad \text{or} \quad SO + OH \rightarrow SO_2 + H \\ SO_2 + O + M &\rightarrow SO_3 + M \end{aligned} \qquad (3.20)$$

SOx also contribute to ozone depletion and acid rain, so their release needs to be limited. Fuel substitution can be used to combat this problem, however, other technologies include abatement or directly removing SOx from gas streams – flue gas desulphurisation, FGD (Speight, 1994). Abatement mechanisms include the use of sorbent injections, often limestone ($CaCO_3$) or a magnesium-calcium salt ($MgCa(CO_3)_2$), which thermally decompose at high temperatures to react with SOx to form gypsum, a saleable product (Speight, 1994). Integrated gasification combined cycles are also efficient at reducing SOx. The control methods, FGD, facilitate the removal of SOx before the gases are released to the atmosphere. Sorbent injections, similar to those described above, use limestone to react with S. Scrubbing processes, either wet or dry, also use a form of injection into the flue gas. Wet scrubbers, although they have many drawbacks, such as poor reagent utilisation, corrosion and deposition, use limestone to remove up to 90 % of SOx (Berkowitz, 1979; Speight, 1994); it is injected into the flue gas, upon which SO_2 is dissolved and undergoes hydrolysis, shown below, after which the dissolution of the limestone occurs, eventually forming a precipitate, which is oxidised to gypsum:

$$\begin{aligned} &\text{hydrolysis: } SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \\ &\text{precipitation: } Ca^{2+} + HSO_3^- + \tfrac{1}{2}H_2O \rightarrow CaSO3{\cdot}\tfrac{1}{2}H_2O + H^+ \end{aligned} \qquad (3.21)$$

Dry scrubbing uses an alkaline solution sprayed into the gases, which dries on reaction with SO_2. This can remove up to 90 % of SOx but is expensive (IEA, 1993). The final control method is the

uneconomical Wellman-Lord process; sodium sulphite (Na_2SO_3) is expensive and the sodium hydrogen sulphite ($NaHSO_3$) product is of nominal value (Berkowitz, 1979; Speight, 1994):

$$Na_2SO_3 + SO_2 + H_2O \leftrightarrow 2NaHSO_3 \quad (3.22)$$

There are also processes for the combined removal of NOx and SOx: SNOx and SNRB – SOx-NOx-ROX-BOX (Coal R&D, 1997). The first is a series of catalytic reactions where NOx are reduced using ammonia and SOx are oxidised to sulphuric acid (H_2SO_4); this can remove up to 95 % of both, although precise temperature control is required. SNRB uses dry lime ($Ca(OH)_2$) and ammonia with a zeolite catalyst to reduce NOx and oxidise SOx at high temperatures. S is not only present in flue gases as SOx; hydrogen sulphide (H_2S) is another problematic acid gas species that requires removal. Other sulphur-containing compounds may also be present, such as mercaptans (thiols), thiophene, disulphides and benzothiophene, though they are usually converted to H_2S by hydrogenation.

HCl is also an acid gas and thus has a corrosive nature; its formation is usually concerned with the incineration of MSW, due to the plastic content, rather than with coal or biomass, unless high percentages of chlorine (Cl) are found in these fuels. This can be removed from flue gases using a wet or dry lime scrubbing, similar to the process for SOx removal described above.

3.4.1.3 Unburned Hydrocarbons, Polycyclic Aromatic Hydrocarbons and Volatile Organic Compounds

UHCs form in fuel-rich environments, due to insufficient oxygen, thus their presence indicates incomplete combustion (Larsen and Larsen, 1998). There are two types: aliphatic and aromatic. The former are non-toxic straight-chain compounds, which form when hydrocarbon fragments polymerise in the flame; this forms a variety of alkanes, alkenes, alkynes, dienes and polyacetylenes. Aromatic compounds with a ring structure are often carcinogenic and some are referred to as PAHs (Larsen and Larsen, 1998). Coal and other carbon-based solid fuels produce aromatic UHCs on incomplete combustion, where the industrial use of coal is one of the main contributors (DEFRA, 1999). Aromatic UHCs and PAHs form when benzene or other rings join during ring-closing mechanisms; multi-ring formation is a two-stage process where an existing ring reacts with diene radicals. They are toxic, contribute to the greenhouse effect by absorbing and reemitting radiation and are a factor in photochemical smog formation. Removal techniques are similar to those for CO, which are also a result of incomplete combustion; they include Pt or Rh catalysts, fuel-lean combustion, ensuring sufficient fuel-oxidiser mixing and avoiding reactions quenching on cold surfaces. Reducing particulate emissions by using a gaseous or liquid fuel can also reduce UHCs.

Volatile organic compounds (VOCs) are products of partial combustion, due to turbulent eddies causing bypassing of the main combustion zones; they are toxic and cause environmental problems, but sufficient mixing aids their reduction (Williams, *et al.*, 2001b).

3.4.1.4 Dioxins and Furans

Dioxins and furans, polychlorinated dibenzodioxins and dibenzofurans (PCDD/F), are a set of ringed compounds with one or more hydrogen atoms replaced with Cl; they are essentially a mix of PAHs and Cl. As they require a source of Cl to form, they are usually associated with MSW incineration, due to the Cl in plastics. It is, however, a trace element found in a range of other fuels. Of the 210 PCDD/F compounds, only 17 are toxic; the most noxious, TCDD, 2,3,7,8-tetrachlorodibenzo[p]dioxin, and TCDF, 2,3,7,8-tetrachlorodibenzofuran (Figures 3.4 and 3.5), have a toxic factor of 1.

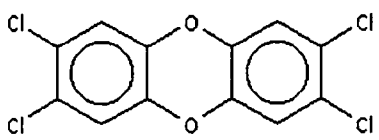


Figure 3.4: The structure of 2,3,7,8-tetrachlorodibenzo[p]dioxin, TCDD – the most toxic known dioxin.
Source: NIST (2005)

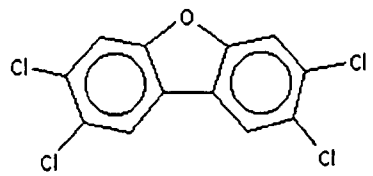


Figure 3.5: The structure of 2,3,7,8-tetrachlorodibenzofuran, TCDF – the most toxic known furan.
Source: NIST (2005)

There are three fundamental reasons for their presence in combustion emissions (Fielder, 1998); some are already in the system and are not destroyed, whereas others form from related Cl-precursors, such as chlorinated benzene rings or polychlorinated biphenyls. The third mechanism is where PCDD/Fs form via a two-staged process, *de Novo Synthesis*, where chemically unrelated compounds react with Cl, at low temperatures (200-400 °C), often on flyash with a metal catalyst. First, Cl is transferred to the C structure and then the oxidation of the C occurs, releasing the PCDD/F as a by-product. These can be removed from flue gases using activated carbon and dry lime scrubbers; they are adsorbed onto these particles, which are then removed using fabric filters. Fuels containing large quantities of S can inhibit the development of these pollutants (Fielder, 1998); low S concentrations in fuels favour PCDD/F formation by allowing *de Novo Synthesis* to occur. The Deacon process, outlined below, occurs, forming molecular Cl gas and renewing the copper chloride ($CuCl_2$) catalyst, with a copper oxide (CuO) intermediate:

$$\begin{array}{r} CuCl_2 + \tfrac{1}{2}O_2 \rightarrow CuO + Cl_2\,(g) \\ CuO + 2HCl \rightarrow CuCl_2 + H_2O \\ \hline 2HCl + \tfrac{1}{2}O_2 \rightarrow H_2O + Cl_2\,(g) \end{array} \qquad (3.23)$$

where the sulphur effectively captures the molecular chlorine (Fielder, 1998):

$$Cl_2 + SO_2 + H_2O \rightarrow 2HCl + SO_3 \qquad (3.24)$$

3.4.1.5 Flue Gas Cleaning: A Post-Combustion Strategy for Gaseous Pollutants

Flue gas cleaning refers to the removal of pollutants from the exhaust before it is released to the atmosphere. It usually involves different phases and processes; particulates are often removed both before and after the elimination of gas-phase pollutants (Figure 3.6). Various aspects of gas cleaning have already been described, relating to specific contaminants; here, a more general review is presented. The techniques are varied and have developed over many years, to now perform specific tasks for a

variety of applications. Speight (1994) suggests several factors that are crucial to consider in the choice of technology: the concentration and species of pollutants, the level of cleaning needed (to meet legislation) and the properties of the gas. There are three primary mechanisms by which gas phase pollutants are removed: adsorption, absorption and condensation. These processes can also be applied to gaseous fuels prior to their use, for gas purification; passing the fuel through one of these systems allows species to be removed that can be problematic later in the process (Berkowitz, 1979).

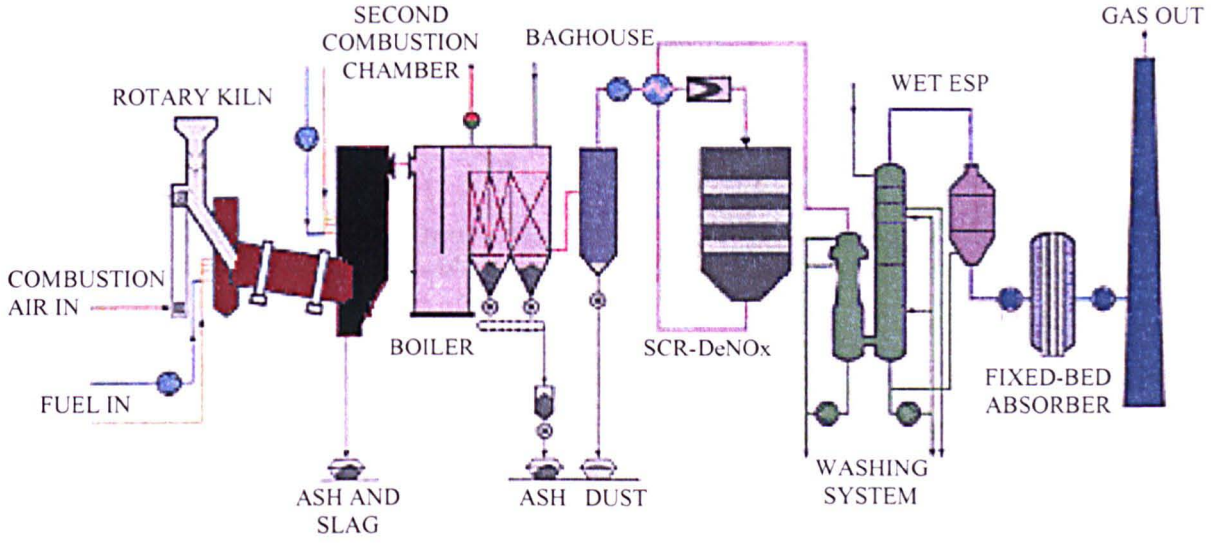


Figure 3.6: The operations in a flue gas cleaning system attached to a rotary kiln.
Source: Donau Carbon (n.d.)

Adsorption removes pollutants by their sorption onto the surface of a solid, which can be physical or chemical depending on whether van der Waals' forces or chemisorption dominates (Speight, 1993). Physical adsorption occurs rapidly, limited by the diffusion rate; chemisorption generally occurs slowly and is often reversible (Speight, 1993). This can eliminate many species, including SO_2, dioxins and furans, but not large hydrocarbons (Speight, 1993). Many adsorbents are available, such as silica gel, zeolite and activated carbon (LeVan, *et al.*, 1997); it is necessary for these to be strong and to withstand attempts to deteriorate their structure. They are thus normally granular and porous, having a large surface area per unit mass (Speight, 1993). Where adsorbents are expensive, it is vital they can be regenerated, by thermal regeneration, pressure and inlet purge, once the adsorbate has saturated the adsorbent.

Absorption is a distinctly different process – it is a method whereby gaseous pollutant molecules diffuse into a liquid across the concentration gradient, due to their differential concentrations. Absorption can be physical (by the dissolution of pollutants), chemical (reactions between the absorber and contaminant) or a combination of both (Edgar, 1983; Speight, 1993). The diffusion rate, and thus removal efficiency, is controlled by varying the surface area of the liquid or manipulating the flowrate and turbulence of the gas; the flowrate of the solvation liquid can also be controlled. Absorption processes occur in towers, categorised as packed columns, spray towers, tray towers or Venturis (Speight, 1993). The most common is the packed column, consisting of a column filled with packing materials resting on a support plate, which does not restrict the gas and liquid flows; they both pass around the packing in a counterflow flow

regime (Fair, *et al.*, 1997). Desorption releases the contaminants, where additions of a neutralising agent are usually required (Speight, 1993). The packing significantly affects operations and thus the appropriate choice is crucial; there are several types, described as structured or random (Figure 3.7). Packing media is made from a variety of materials, such as plastic, metal or ceramics and are chosen based on their properties and suitability. Wet and dry absorption can treat SOx.

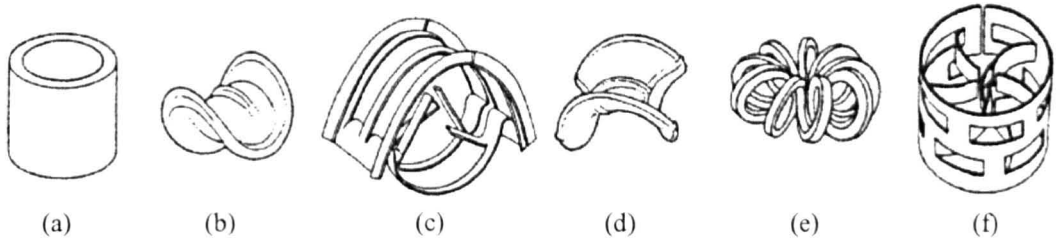


Figure 3.7: Examples of different types of random packing for packed columns: (a) Raschig ring, (b) Berl saddle, (c) metal Intalox, (d) ceramic Intalox saddle, (e) Tellerette and (f) Pall ring.
Source: Fair, *et al.* (1997)

Compressing and condensing gases is the last mechanism for removing gaseous pollutants; the principle of this operation is that temperature reductions or pressure increases in a closed system cause polluting species, particularly acid gases, to condense out. The two methods, categorised as dynamic or positive displacement compressors, each have specific applications. It is important that the gases are compressed prior to condensation to avoid damaging the compressor. High pressure is of course expensive, but increasingly rigorous legislation concerning emissions limits now often necessitates its use.

3.4.2 Particulate Emissions

3.4.2.1 Characterisation of Particulates

Particulates are fine (0.01-50 μm), solid particles often emitted in the effluent gases during industrial processes, such as combustion (Grainger and Gibson, 1981). The removal of these solid-phase emissions is essential to minimise the amount entering the atmosphere, as their release can be extremely problematic (Orr, 1966). Airborne particulate matter has both an effect on the environment and human health. Their release can induce light scattering, which is able to alter the climate, through the formation of cloud condensation nuclei, and reduce visibility (Davidson, *et al.*, 2005; Andreae and Rosenfeld, 2008). Furthermore, the presence of particles in the air can reduce its quality and when inhaled, can cause a range of respiratory and cardiovascular illnesses (Seaton, *et al.*, 1995; Davidson, *et al.*, 2005).

The composition of particles depends on their source and if it is a thermal treatment process, then also on the fuel. Whilst the vast majority will be ash (flyash), some fuel particles may have escaped unburned. The formation of particulates can be avoided completely with the use of a gaseous or liquid fuel. Many elements initially in the fuel are concentrated in the ash, particularly metals. Alkali metals, such as Na and K, which are often found in biomass, can cause difficulties to the operating system, through slagging and fouling; the Alkali Index indicates the potential fouling for a particular fuel (Jenkins, *et al.*, 1998).

Hg is another problematic metal, released in gaseous form and as fine particles, which are potentially hazardous and highly toxic; the main source of anthropogenic emissions is from coal combustion (Valković, 1983; Swaine, 1990; Huang, *et al.*, 2004; Senior and Johnson, 2005; Yudovich and Ketris, 2005). Hg can be removed by extraction from fuels prior to combustion or from the flue gases.

3.4.2.2 Removal of Particulate Matter

As seen in Figure 3.7, the removal of particulates can occur both prior and subsequent to the elimination of gaseous pollutants. The main types of cleaning equipment – electrostatic precipitators (ESPs), wet scrubbers, fabric filters and cyclones – will be briefly reviewed here (Figure 3.8). Each caters for a range of specific purposes and are compared by Edgar (1983) and IEA (1985).

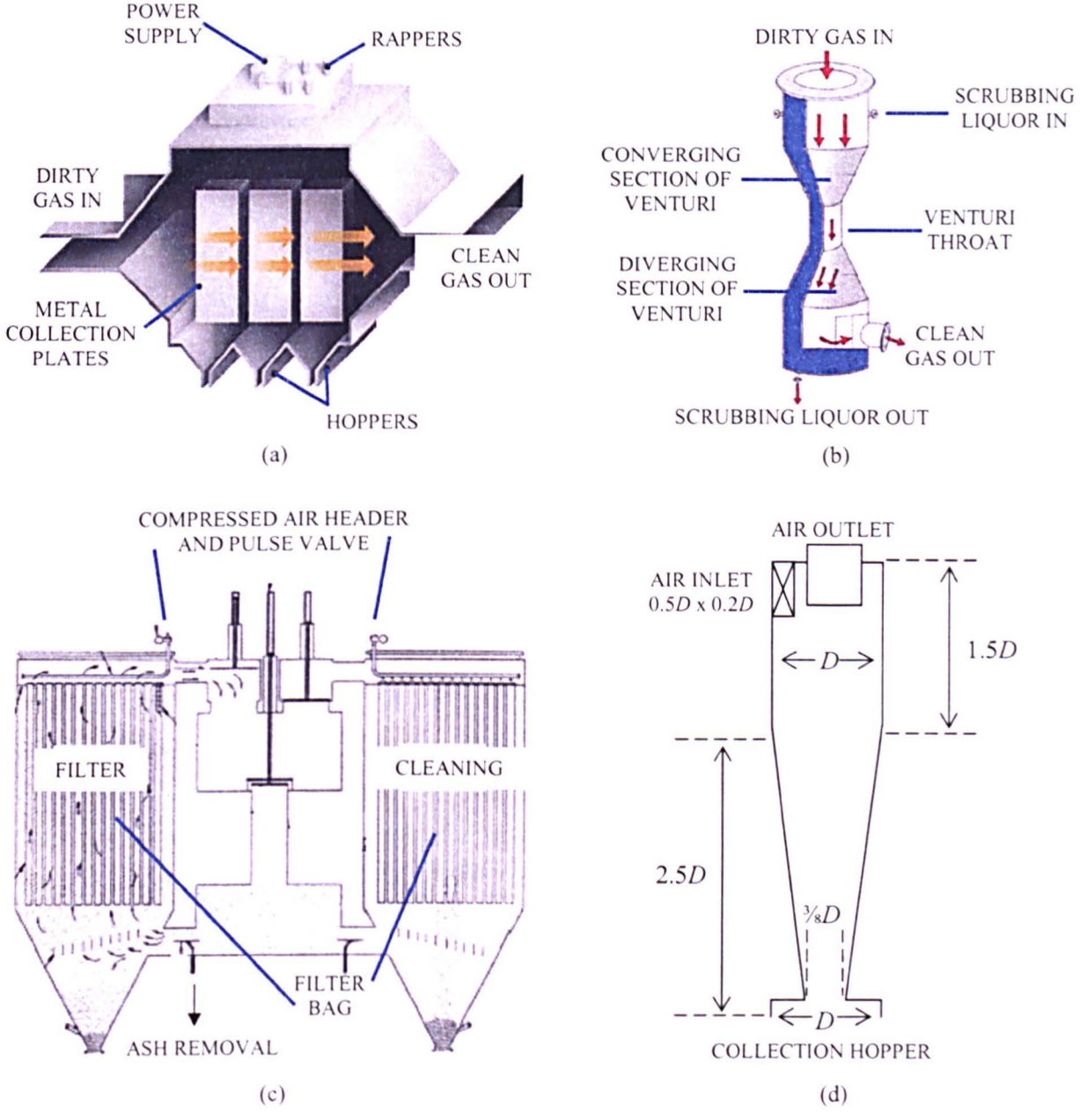


Figure 3.8: Particulate removal methods: (a) electrostatic precipitator; (b) Venturi scrubber; (c) fabric filter; and (d) high-efficiency cyclone, dimensions with respect to the barrel diameter, *D*, 0.612 m. Sources: (a) Dayley and Holbert (2003); (b) Pacific Consultants and Engineers (n.d.); (c) Bundy Environmental Technology (1999); (d) Stairmand (1972) and Clift (1997).

ESPs remove particles by applying electrical forces to electrodes and are classified on whether the corona, the charge produced by free electrons, is positive or negative (Figure 3.8a). Collection occurs in four stages: particle charging, precipitation, agglomeration and cleaning. Problems associated with their use include broken or distorted electrodes, corrosion, back corona and sparking (Speight, 1994). The costs and efficiency of ESPs and other gas cleaning technologies are compared in Table 3.3.

REMOVAL METHOD	COSTS		EFFICIENCY
	INITIAL	OPERATING	
ESPs	high	moderate	~99 % for < 1 μm
Fabric Filter	moderate	moderate	up to 99.9997 %
Venturi	low to moderate	can be high	98 % for 1 μm
Cyclones	low	low	up to 99.99 % for 5 μm

Table 3.3: The costs and efficiencies of particulate removal methods.

Wet scrubbers use a wetted surface or distributed liquid to remove particles; water is often used as the scrubbing liquid. There are many types of scrubbers; the most common and efficient is the Venturi (Figure 3.8b). Collection is mainly by particle inertia and is thus a function of particle mass, although there may be some negligible impaction (Speight, 1994). The main issue relating to scrubbers is that the removal of a particulate problem leads to the formation of a liquid effluent, which then requires clarification and cleaning (Stairmand, 1972; Arrowsmith and Ashton, 1997).

Fabric filters comprise porous textile media, which collect particles in the passing gas (Figure 3.8c). This builds up over time forming a 'cake' and the medium requires regular cleaning to remove this; systems are categorised by their cleaning mechanism: pulse jet, reverse flow or shaking method (Stairmand, 1972; Morris and Allen, 1997). The fibres used are either woven or felted, with a variety of finishes to suit a specific purpose.

There are three main types of cyclone: reverse flow, uniflow and multi-cyclones, which operate on the principle that a spiralling gas vortex subjects particles to a centrifugal force, where collection is by particle inertia (Speight, 1994). These are often used as primary collectors before other treatments due to their often low collection efficiency, although efficiencies are improved by increasing the entrance velocity or pressure drop, or decreasing the vortex finder diameter, as in the high-efficiency design of Figure 3.8d (Stairmand, 1972; Clift, 1997). There are also several problems associated with many cyclone designs; erosion, solids build-up and vibration are detrimental to the equipment and re-entrainment through gas leakage or from the wall and hopper also pose challenges to the efficiency.

3.4.3 Specificities of Coal Tailings and Spent Mushroom Compost

This section describes the pollutants that may form during the thermal treatment of coal tailings and SMC, based on literary information, particularly their compositions. This will be considered further during the experimental determination of material composition.

CO_2 release is problematic for the combustion of all fuels, though carbon sequestering and other capture and storage technologies are being developed. The ultimate analysis for SMC (Table 2.11) identified additional elements that may lead to pollutants, such as N, S, Cl and P. Williams, *et al.* (2001a) showed that although the amounts of N and S are high, they are in inorganic forms (nitrates and sulphates, such as gypsum) and thus NOx and SOx will be minimal if combusted in a fluidised-bed. These compounds only decompose at extreme temperatures, for example 1450 °C for gypsum, which are unlikely to be generated here (Williams, 2001). Chugh and Patwardhan (2004) found that NOx and SOx emissions from coal tailing combustion were also low. Thermal NOx could still form however if air is used in the combustor. Williams, *et al.* (2001a) posited that most Cl and P should remain as chlorides and phosphates in the ash, although some HCl may form from SMC combustion. Williams (2001) measured the emissions of various pollutants from SMC combustion, concluding that the VOC concentration was low enough to not be problematic. There are significant proportions of Ca from the lime in the casing layer; when co-firing with coal tailings, however, it may be useful in capturing S and reducing SOx (Altun, *et al.*, 2006). The high S content may inhibit *de Novo Synthesis* to minimise dioxin and furan formation (Fielder, 1998). Although coal tailings are different from coal, the trace elements and thus pollutants are often similar, such as alkali metals, which can contaminate ash and cause fouling and slagging; individual samples should be analysed to gain an accurate description of the likely emissions. In addition, alkali metals are often found in biomass.

A further disadvantage is that the materials contain significant proportions of ash (Tables 2.11 and 2.16), which would remain after combustion and is often entrained in flue gases. Particulate removal devices, such as those described above, will be needed to minimise their release. Ash disposal could be minimised through its use as an activator for PFA or recycled to the construction industry (Russell, *et al.*, 2005).

3.5 SUMMARY

Thermochemical processing techniques for fuels were discussed, including combustion, gasification and pyrolysis, which are key processes by which biomass is used. The main chemical reactions were outlined, which can later be compared to the results of experimentation conducted. Many detrimental emissions associated with the thermal treatment of fuels apply to the use of coal and biomass; the formation and effects were described and evaluated for CO, CO_2, NOx, SOx, HCl, UHC, PAH, VOC, dioxins and furans. Subsequent removal strategies were reviewed, such as SCR or SNCR for NOx and FGD for SOx. If enough money is available, the majority of these pollutants can be removed, limiting their negative environmental and health impacts. These removal strategies were generally flue gas cleaning methods, where pollutants are removed before release to the atmosphere. Particulate removal was also considered and various collection techniques were assessed, where ESPs and fabric filters were the most efficient. Specific pollutants relating to the use of SMC and coal tailings were identified; these included ash, alkali metals, NOx, SOx and CO_2, although these can be reduced by cleaning the flue gas. Their removal may also reduce the risk of slagging, fouling and other operating problems.

4

FLUIDISATION THEORY

4.1 INTRODUCTION

Combustion, discussed previously in Section 3.2.1, can occur in many reactors, one of which is a fluidised-bed. There are many varieties of fluidised-bed combustors and an overview of the two main types is presented here. The main operating principle – fluidisation – is considered, culminating in a contemplation of its relative merits, both generally and with specific reference to combustion. This fluidisation phenomenon occurs when fluid flow through a bed of solid particles causes them to expand and take on the properties of a fluid. Fluidisation theory within reactors is another important aspect; topics, such as fluidising velocity, transport disengagement height and pressure drop are examined. The characterisation of fluidised particles is also considered, focussing on their properties and classification. Lastly, examples of biomass combustion in fluidised-beds are explored.

4.2 FLUIDISED-BEDS AND THEIR OPERATION

4.2.1 Types of Fluidised-Bed

A range of equipment can be used to burn fuels, depending on whether heat and/or energy is the required end product. These vary from small-scale domestic systems to large-scale power stations and include furnaces and packed-beds among others (McKendry, 2002b). The fluidised-bed is one of the most common combustors, which consists of a bed of fluidised particles, frequently sand, with a freeboard above. There are many types of fluidised-bed reactors that are used, including circulating, bubbling and turbulent bed reactors, as well as atmospheric or pressurised designs, of which the main types used for combustion are discussed herein.

A typical fluidised-bed system for a combustion operation consists of the following components: a combustion vessel, a distributor plate upon which the solid particles sit, a start-up system/ignitor with auxiliary fuel, primary (fluidising) and secondary air supplies, fuel handling and feeding mechanisms and fly and bottom ash collection systems. Often, some form of gas clean-up is also employed to remove particulates and reduce the quantities of harmful gaseous emissions that are released to the atmosphere to comply with relevant legislative policies. The primary purpose of fluidised-bed combustion is that fuel pellets or chips burn in the bed and are not carried out with the flue gases; this increase in density improves the energy efficiency (Holm, *et al.*, 2006).

Circulating fluidised-beds differ from bubbling-bed designs due to the recirculation of bed particles, which generally expand more than for bubbling designs, described below (Howard, 1989). These operate at high fluid velocities to achieve particle fluidisation and recirculation. A continuous flow of particles are provided to the bed, due either to the collection and returning of particles entrained in the exhaust gases using a cyclone (Figure 4.1) or using an inclined distributor plate; to maintain a constant bed mass, the return rate of the particles must be equivalent to the rate at which they elutriate (Highly and Kaye, 1983; Howard, 1989). This 'fast' fluidisation ensures the heat and mass transfer rates between the fluid and the particles are sufficiently high and the temperature distribution is even (Howard, 1989). External heat exchangers are common for such combustors, to increase operational flexibility (Valk, 1986).

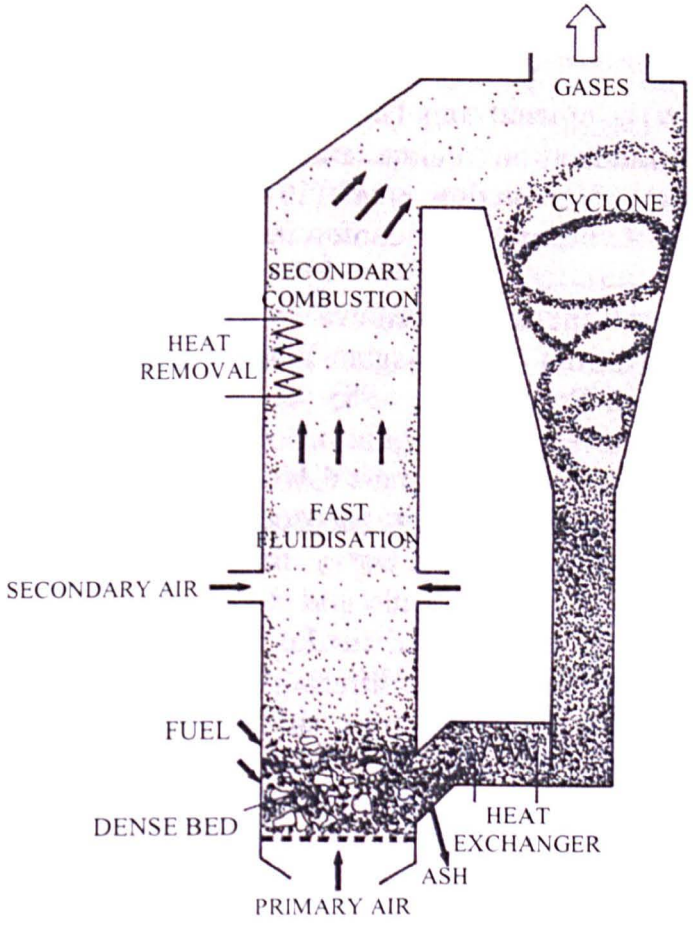


Figure 4.1: A circulating fluidised-bed combustor, using a cyclone to capture and recirculate particles. Source: Howard (1989)

Bubbling fluidised-beds also consist of the components described above. For most designs, the solid bed of particles sits upon a perforated/porous base plate or one with nozzles, known as a distributor, and the fluid enters the vessel through the orifices to fluidise the particles. The primary combustion air is generally used as the fluidising air, whereas secondary air jets are usually located further up the vessel, to ensure complete burnout throughout the reactor. To initiate combustion, the bed must be heated as well as fluidised, and thus gaseous fuel is usually introduced to perform this function; once the bed is sufficiently heated and fluidised, the fuel can be introduced. Over-bed or in-bed feeding systems are employed and once the fuel is combusted, the bottom ash remains in the bed and the flyash is removed with the exhaust gases. A cyclone for particulate removal is usually included within the system before the exhaust is cleaned to remove gaseous pollutants. When these are used for energy recovery, heat transfer and recovery systems are incorporated towards the top of the reactor.

4.2.2 Overview of the Principle of Fluidisation

The primary operating principle of fluidised-beds is fluidisation, usually using a gas, frequently air, or sometimes a liquid. This phenomenon is caused by the resistance between the particles and the fluid passing through them (Botterill, 1983). As the gas passes through the bed, often sand, it is able to convert the solid particles into a suspended and expanded mass, which exhibits the properties of a liquid; this reduces the resistance as the particles move freely (van Swaaij and Prins, 1986; Pell and Dunson, 1997). These particles sit on the plate towards the bottom of the vessel, as described above. If the air flowrates are below the critical value for the system, complete fluidisation will not occur, whereas if the air flowrates are above the threshold, bubbles will form within the sand bed (Pell and Dunson, 1997). Bed expansion is often not uniform when a gas is used and consequently instabilities (bubbles) form in the bed (Howard, 1989). If expansion and fluidisation are more uniform, the mixing is also more even and thus heat transfer during combustion is more constant (Valk, 1986).

The advantages of using a fluidised-bed include effective solid-fluid contacting without mechanical components due to the large particle surface area in contact with the fluid and the comparative ease with which fluidised particles can be handled (Botterill, 1983). The benefits for combustion in these systems are that the processes are more stable and can occur at greatly reduced temperatures, which are uniform, compared to other reactors (Radovanović, 1986); this ensures that the occurrence of cold- or hot-spots within the furnace is very much reduced, lowers excess air requirements, results in significant reductions in pollutants, specifically NOx and SOx, and fouling, corrosion and ash fusion are less common. The gas used for fluidisation is often air and thus can be utilised as both the fluidisation air for the sand bed and the combustion air for the fuel. The use of higher energy density fuels, i.e. fuel pellets, directly improves the energy efficiency in a fluidised-bed system, as the densified fuel burns within the bed and minimises the number of small and/or light particles that may be carried up through the freeboard with the fluidising/combustion air and would otherwise escape unburned with the flue gases (Saenger, *et al.*, 2001; Holm, *et al.*, 2006).

The drawbacks, however, are that the operating conditions are limited to the range where the bed is fluidised, there is often potential for erosion and the cost of providing the fluid at a pressure to achieve fluidisation is frequently high. As discussed below, there are also limitations concerning the particles that can be used in fluidised-beds. The disadvantages concerning combustion are that N_2O often forms due to the lower combustion temperatures and processing is often required for the fuel – pelletisation or chipping to ensure particles are heavy enough to combust within the bed.

4.3 FUNDAMENTAL FLUIDISATION THEORY

A number of factors need to be considered concerning the design and operation of fluidised-bed systems. These theoretical topics include the minimum and maximum fluidising velocity, pressure drop, terminal velocity and the transport disengagement height; these are all discussed here.

4.3.1 Minimum and Maximum Fluidising Velocities and Pressure Drop

The fluidising velocity is the speed at which the gas, or liquid, flows through the packed bed to initiate fluidisation. There are five key stages in the behaviour of the bed as the fluidising velocity is increased. These are: (i) when the bed remains packed; (ii) the occurrence of incipient fluidisation; (iii) bubbling of the bed starts; (iv) slugging of the bed ensues; and (v) entrainment of the bed begins (Botterill, 1983; Howard, 1989). In the first phase, the bed does not change a great deal as the gas initially flows through it. A pressure drop (ΔP in N/m^2) can be observed, caused by the loss of mechanical energy due to the friction between the particles and gas (van Swaaij and Prins, 1986); as the gas velocity increases, the ΔP across the system rises, the magnitude of which depends on the gas and particle properties. As the gas flowrate increases further, the second behavioural phase is achieved, as the incipient fluidisation of the particles occurs once the minimum fluidising velocity (U_{mf} in m/s) is reached; this minimum gas flow required to fluidise the bed sufficiently is expressed as:

$$U_{mf} = \frac{\dot{V}_{mf}}{A} \tag{4.1}$$

where $\dot{V}_{mf}$ is the volumetric flowrate (in m^3/s) at the initiation of fluidisation and A is the cross-sectional area of the bed, in m^2 (Howard, 1989). In practice, the fluidising velocity is usually greater than the minimum fluidising velocity. For U_{mf} to be reached and the appropriate pressure drop to be achieved across the bed, the force of the gas must be at least equal to the weight of individual sand particles and thus high velocities are often required. The pressure drop across the distributor can be calculated from the condition when the total particle weight can be supported by the flow, hence:

$$\Delta P = \frac{m}{\rho_p A} (\rho_p - \rho_f) g \tag{4.2}$$

where m is the mass of the particles, in kg, ρ_p and ρ_f are the density of the particles and the fluidising gas (or liquid), in kg/m^3 and g is the gravitational acceleration, in m/s^2 (Botterill, 1983; Howard, 1989). For particle sizes greater than 150 μm in diameter, inertial forces become increasingly important, where the Ergun equation can be used to aid the establishment the U_{mf}:

$$\frac{\Delta P}{h} = \frac{150(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu U}{(\varphi d_p)^2} + \frac{1.75(1-\varepsilon)}{\varepsilon^3}\frac{\rho_f U^2}{\varphi d_p} \quad (4.3)$$

where h is the height of the bed above the distributor (in m), ε is the void space in the bed, μ is the fluid viscosity (in Ns/m^2), U is the fluidising velocity (in m/s), φ is the particle sphericity and d_p is the mean bed particle size (in μm). The distributor plate and the rest of the system are usually designed for a specific ΔP (van Swaaij and Prins, 1986). Once incipient fluidisation is achieved, however, the ΔP does not increase further, but the bed expands as particles are rearranged to increase bed voidage. As the gas velocity increases, phase three occurs when the temperature and composition of the bed become somewhat more homogeneous; this is usually accompanied by the presence of sufficient but non-uniform bubbles. By increasing the fluidising gas velocity further, phases four and five can be achieved, upon which slugging of the bed and subsequent particle entrainment occur respectively. Both cause severe pressure fluctuations across the bed, until so much of the bed has been entrained that the pressure drop decreases. The behaviour of particles fluidised using a liquid instead of a gas is somewhat different, particularly when fluidising velocities above those inducing incipient fluidisation are used (Howard, 1989). As fluidised-bed combustion is the focus here, fluidisation using liquids is not considered further.

4.3.2 Terminal Velocity, the Transport Disengagement Height and Elutriation

When the terminal velocity (U_t in m/s) is achieved at high fluidising gas velocities, particles within the bed can move out into the freeboard. When the Archimedes number (a dimensionless number defining the fluid motion from differential densities) for the fluid is low, below 200, the terminal velocity can be defined as (Broughton and Howard, 1983):

$$U_t = \frac{\rho_p d_p^2 g}{18\mu} \quad (4.4)$$

The U_t can be computed for the smallest particle size and provides an indication of the maximum gas velocity that should be used (Howard, 1989). If the fluidised-bed is operating at velocities which exceed U_t, particularly if this is based on the smallest instead of the mean particle size, the bed will lose material; particles elutriate into the freeboard, entrained by the gas, especially those whose U_t is small compared to their U (Howard, 1989). Homogeneous fluidisation occurs between the U_{mf} and U_t of the particles (van Swaaij and Prins, 1986). Systems are often in place to capture and return these elutriated particles to the bed, however, this is often the arrangement used to recirculate particles in circulating fluidised-beds.

A related concept to U_t is the transport disengagement height (TDH), which is the distance above the bed at which particle entrainment and elutriation become constant, sometimes known as the transport disengagement zone (Pell and Dunson, 1997). This TDH is also the term used to describe the sufficient height of the freeboard to limit the amount of particles that are lost; these two different definitions are sometimes referred to as the TDH_C and TDH_F respectively, for coarse ($_C$) and fine ($_F$) particles (Howard, 1989). It is therefore vital that enough freeboard height is provided to ensure that any disengaged particles above the surface of the bed will fall back to the bed from the gas stream (Howard, 1989). This

ensures that particles are not lost from the system and carried out with the gas emissions. This elutriation only occurs at extreme velocities, caused particularly by bubbles bursting at the surface, which is especially true for fine particles (Botterill, 1983). Providing a sufficient TDH is necessary for appropriate solid loading and size distribution within the fluid; it is also important that heights which dramatically exceed the TDH are not used, as this not only increases the cost of construction, but also the height needed to house the vessel (Howard, 1989).

4.4 CLASSIFICATION AND PROPERTIES OF PARTICLES

Even with the most appropriate conditions, not all particles can be fluidised, and of the ones that do, diverse behaviour is noticed between particles of different characteristics (Howard, 1989). Geldart (1972, 1973) therefore classified particles according to their properties and the way in which they behave during fluidisation; this characterisation is based primarily on their size and density in relation to the fluid. Other physical properties of the particles that are of particular significance include sphericity and the void space the particles form in the bed.

4.4.1 Classification of Solid Particles

Geldart's classification scheme of particles fluidised by gases is based on the mean bed particle size (d_p) and the density difference between the particles and the fluidising gas (ρ_p - ρ_f), of which there are four different categories: A, B, C and D (Geldart, 1973; Howard, 1989). As can be seen from Figure 4.2, these four categories of particles fit into the classification diagram. These will be considered with increasing particle size, starting with Category C particles.

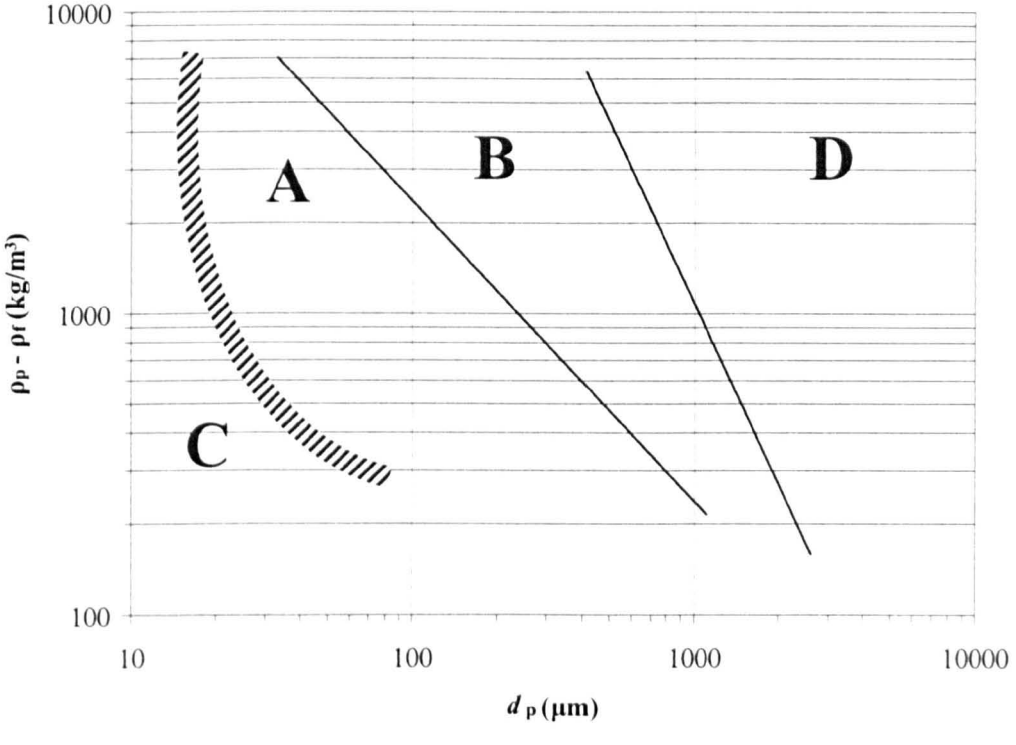


Figure 4.2: Geldart classification of powder.
Source: Adapted from Geldart (1973) and Howard (1989)

Category C particles are small (d_p < 30 μm) and/or are of low density, although cohesive particles also fit into this category (Geldart, 1973); often, particle sphericity, explored below, is not very high (Yates, 1983). Due to this, the interparticle forces are too strong, greater than gravity, and thus such particles are extremely difficult to fluidise completely (Botterill, 1983; van Swaaij and Prins, 1986). When fluidisation of these particles is attempted with a gas, specific channels are usually formed, where the resistance of the gaseous flow is particularly low and therefore most of the flow passes through these pathways (Howard, 1989); this is known as channelling (Yates, 1983). Accordingly, the distribution of the gas and particles is often not uniform and fluidisation is rarely achieved – the particles remain fairly static and the pressure drop does not generally reach the critical value where it equals the unit weight of the bed (Botterill, 1983; Yates, 1983). Further increases of gas velocity only enlarge the channels. To improve the possibility of 'normal' fluidisation, mechanical stirrers or vibrators can be utilised to break down the channels and redistribute the bed (Geldart, 1973).

Category A particles are slightly larger (d_p = 30-150 μm) and/or are denser (ρ_p < 1500 kg/m^3) than Category C, and are usually referred to as powders (Howard, 1989). These particles allow homogeneous, stable dense-phase bed expansion, thus uniform fluidisation can occur throughout once U_{mf} is reached and before bubbles are seen (Geldart, 1973; Botterill, 1983; Yates, 1983). The minimum bubbling velocity is greater than the U_{mf} and where the bubbles coalesce, axisymmetric slugs are common (Yates, 1983). Bubbles start to appear in the bed once values much greater that the U_{mf} are achieved for the overall fluidising velocity; these bubbles form easily but the maximum stable bubble size tends to be quite small (Yates, 1983).

Category B particles allow only moderate fluidisation to occur, as they are larger (d_p = 150-500 μm) and denser (ρ_p = 1500-4500 kg/m^3) than those in the previous category. Bed expansion is generally smaller and significantly less stable, where bubbles (aggregative fluidisation) occur at much lower fluidising velocities, often at, or slightly above, U_{mf} (Geldart, 1973; Botterill, 1983; Howard, 1989). The pressure drop across the bed is usually adequately high to ensure stable operation (Geldart, 1972). There is generally little interaction between particles, compared to Category A (Yates, 1983).

Category D particles are considerably larger (d_p > 600 μm) and/or denser than those in the preceding categories; this necessitates the use of much greater fluidising velocities to achieve fluidisation and subsequently, the gas flow becomes somewhat turbulent, compared to the laminar flow of other categories (Howard, 1989). Any bubbles that form travel slowly to the bed surface (Yates, 1983).

4.4.2 The Physical Properties of Fluidising Particles

The physical properties of particles, such as their density and size, are among a variety of factors that critically effect fluidisation and are important in determining the above variables. In addition to these properties, their size distribution, shape, surface area and bed voidage are also important.

Particle size and shape have a significant influence on fluidisation by impacting bed packing and void space. Particle shape ranges considerably, where the majority of particles are irregular, not spherical. The shape of non-uniform particles is quantified by determining their sphericity, φ:

$$\varphi = \frac{\text{surface area of sphere of the same volume as the particle}}{\text{surface area of particle}} \tag{4.5}$$

As most particles are not uniform, their sphericity is low, although some, such as sand, can have quite high φ values (φ = 0.92-0.98), and therefore are almost spherical (Howard, 1989). A related concept is the effect of the surface area of particles, which has also been previously considered; solid-fluid contacting in fluidised-beds is very effective due to the large total surface area, which enables efficient heat transfer (Botterill, 1983). The surface area is also important as this creates the pressure drop across the bed, due to the fluid flow around the particles.

The particle size distribution, which can be described using a variety of measurements, also effects fluidisation. If this is large, the bed may not be entirely supported by the fluid flow, as the pressure drop achieved may not be equal to the weight of the bed (Botterill, 1983). Further to this point, particle segregation can occur, resulting in different packing characteristics, which can severely influence combustion (Broughton and Howard, 1983). Additionally, if there are some small particles, when elutriation occurs, these particles can escape with the fluid flow and over time, only the larger particles will remain in the bed, thus changing the particle size distribution; furthermore, attrition and fragmentation of particles due to thermal stresses can alter the particle sizes and their distribution, increasing the proportion of fines, as these processes are unlikely to occur uniformly (Botterill, 1983; Howard, 1989). This can accordingly change the heat transfer rate, as well as the gas cleaning mechanisms that are applied (Broughton and Howard, 1983). The particle size distribution is also related to the voidage in the bed; if there is a large range of particles sizes, the smaller particles can fit into the gaps created by the larger ones (Howard, 1989).

The void space in the bed, ε, is the proportion of the bed not occupied by solid particles, but the space between them; this is dependent on the shape and size of the particles and their arrangement in the bed, among other factors (Howard, 1989). Although theoretical determinations of ε are possible, they are often unreliable due to the fact that it assumes that all bed particles are of the same size and shape, as well as the same porosity; in practice, this is of course a somewhat inaccurate assumption and thus predicted values of ε are erroneous. Experimental determination of this is required, by:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_p} \tag{4.6}$$

where ρ_b is the density of the bed, in kg/m^3. Although it has been reported that bed temperature does indeed influence voidage, there is not straightforward expression for this; as particle size increases, this impact is thought to be less important when the flow is turbulent (Botterill, 1983).

4.5 COMBUSTION OF BIOMASS IN A FLUIDISED-BED

Combustion in a fluidised-bed is a common way of obtaining energy; a variety of both non-renewable (fossil) and renewable fuels are used for this application. van den Broek, *et al.* (1996) provided an overview of power generation from biomass combustion. Through comparing a number of technologies, it was concluded that fluidised-beds, particularly circulating systems, are able to combust a range of fuels, often at high efficiency, with good carbon burn-out and low NOx emissions from thermal sources, due to the lower combustion temperatures. Furthermore, SOx concentrations may also be minimal and acid gas retention in the bed can be increased with lime. Here a variety of biomass and waste fuels are considered, the study of which primarily aims to: (i) determine the environmental and technical merits of specific fuels, (ii) establish optimal operating conditions, (iii) investigate co-combustion with a fossil fuel, usually coal or peat, and (iv) characterise and deal with the emissions and ash produced. In addition, modelling work has also been carried out on various aspects of this research area.

In addition to the various aspects of biomass combustion in fluidised-beds that have been investigated, gasification reactions can be carried out as well and thus have also been a focus for studies over recent years. Gasification experiments have been performed for the following types of biomass: waste from the olive oil industry (Garcia-Ibanez, *et al.*, 2004; Andre, *et al.*, 2005), dried sewage sludge (Manya, *et al.*, 2006), eucalyptus red gum wood chips and commercial wood pellets (Ross, *et al.*, 2007). Various aspects of this have been investigated, including a study of the catalytic cracking of tar from Swedish birch gasification using haematite (Nordgreen, *et al.*, 2006), the process fundamentals for fluidised-bed gasification of coffee grounds (Murakami, *et al.*, 2007) and the fate of fuel-nitrogen for birch, *Salix*, miscanthus and reed canary grass during fluidised-bed gasification (Yu, *et al.*, 2007).

4.5.1 Technical and Environmental Merits of Particular Fuels and Establishing Optimal Operating Conditions

The primary reason for investigating the fluidised-bed combustion of biomass and wastes is to determine its technical feasibility and often to also analyse the environmental impacts; furthermore, the ideal operating conditions can be determined. McIlveen-Wright, *et al.* (2001) investigated the combustion of wood in circulating fluidised-beds. A variety of factors were investigated to determine which were the most significant on impacting the economics and efficiency; the former was effected primarily by the discount cash flow rate and the level of afforestation, whereas the moisture content of the fuel and the conditions of the steam cycle were found to have the largest influence on the latter. Medium-sized plants (500 dry tonnes/day) would be economically-viable, while large plants (capacity > 1000 dry tonnes/day) would be competitive with coal-fired power stations. Energy crops, such as alder, poplar and willow had been planted for this purpose; whilst these woods are suitable, they need to be widely available at an appropriate cost and supplied from sustainably-managed forests. McIlveen-Wright, *et al.* (2006) also investigated the technical and environmental viability of co-combustion and co-gasification of coal, biomass and plastic waste; this will be discussed further below, when co-firing is considered.

Other investigations have been completed on coffee and rice husks. Saenger, *et al.* (2001) used single particle combustion techniques and fluidised-bed combustion in a pilot-scale reactor to examine the combustion mechanisms of two different coffee husks. The fuel had a low ash and fixed carbon content, with a high proportion of volatiles (65-72 %); pyrolysis and devolatisation began at low temperatures (170 °C) and for over-bed feeding systems, caused very high temperatures in the freeboard where they burned. An advantage of coffee husk combustion was the low SOx emissions produced. There were however three main disadvantages: (i) NOx emissions were very high and thus reduction technologies will be required; (ii) the ash had a low melting point due to the K_2O (36-38 %) in the fuel, which caused ash sintering, agglomeration, slagging, fouling and corrosion leading to increased costs and maintenance; and (iii) the low bulk density meant the fuel did not necessarily burn within the bed. As briquetting of this material to increase its density was deemed unsuitable, it would be necessary to use the fuel near the production area otherwise high transportation costs would ensue.

Both Armesto, *et al.* (2002) and Rozainee, *et al.* (2008) have examined the fluidised-bed combustion of rice husks, an agro-industrial waste with a high production rate in particular regions. The former performed experimental work in an atmospheric bubbling fluidised-bed to explore combustion behaviour. High combustion efficiencies (in excess of 97 %) could be achieved. The temperature at which combustion occurred and U_{mf} required significantly influenced both this and the CO concentration of the exhaust gas. As the temperatures increased, the combustion efficiency also increased; the CO concentration peaked at 860 °C. Increases in the U_{mf} resulted in reduced combustion efficiency and higher CO concentrations. Bottom ash samples were analysed and were found to contain quartz and haematite, with increasing proportions of potassium-calcium silicates as the time between changing the bed increased; this may also cause agglomeration of the bed. Furthermore, the analysis of the flyash collected from the cyclone revealed the presence of corrosive sylvites. Most of the K_2O was also found here. Rozainee, *et al.* (2008) further investigated the effect of the fluidising velocity during rice husk combustion in a fluidised-bed and used their experimental results to determine an optimum value for this parameter in terms of minimising the carbon in the amorphous ash; this is explored further below, where other ashes from fluidised-bed combustion are considered.

4.5.2 Co-Combustion of Biomass with Other Fuels

Co-combustion of biomass and a fossil fuel is also common, which reduce overall CO_2 emissions compared to coal alone, but can also reduce the efficiency (McIlveen-Wright, *et al.*, 2007). Despite this, the use of biomass and (organic) wastes in this way is often the most economically-viable, as coal combustion mechanisms are well understood, whereas biomass is less so (Armesto, *et al.*, 2003; Gayan, *et al.*, 2004). Fluidised-beds are suitable for this application, as they are able to burn a range of fuels, as stated above (van den Broek, *et al.*, 1996). Furthermore, fluidised-beds can minimise SOx emissions and, as stated by van den Broek, *et al.* (1996), this is integral, especially for co-firing biomass and fuels with high sulphur contents, such as coal. The study by Huang, *et al.* (2006) focussed on modelling the

technical and environmental implications of co-firing coal with a range of biomasses (olive pits, miscanthus, willow chips, switchgrass and straw) in a pressurised fluidised-bed. Combustion parameters for the tests included coal:biomass ratios of 100:0 to 60:40. The co-firing ratio and the characteristics of the fuels were the main factors to impact the overall efficiency, which decreased when biomass was added to the fuel blend, most significantly for the willow chips, which had a high moisture content, resulting in lower combustion temperatures. This however, coupled with the low nitrogen content of the fuel, was also significant in reducing NOx emissions. For the other fuels, NOx concentrations increased, whereas SOx were reduced, as was the net CO_2.

Armesto, *et al.* (2003) studied the feasibility of the co-combustion of lignite and anthracite coals with an olive oil industry residue – foot cake – in a bubbling fluidised-bed. Although the foot cake had a high alkaline content and significant moisture, successful combustion was achieved. It was noted that altering the type of coal, the share of the foot cake and the combustion temperature impacted the emissions; SO_2 and NOx were reduced, although there were increases in the N_2O in the flue gases, due to the lower flame temperatures brought about by the increased moisture levels from the foot cake. There did not appear to be a significant effect on the combustion efficiency with increasing foot cake additions.

Gayan, *et al.* (2004) examined the co-combustion of sub-bituminous coal and lignite with a pine bark forest residue. A variety of operating conditions were considered, including the air velocity, percentage of secondary air (10-35 %), excess air used (18-25 %), temperature (800-900 °C), percentage of biomass in the fuel (0-100 %) and the type and particle size distribution of the coal. The main findings were that carbon combustion efficiency could be improved by increasing the percentage of biomass, using higher temperatures, lowering the fluidising air velocity, increasing the excess air or decreasing the secondary air. The combustor was modelled and subsequently validated using the experimental data. This was able to predict the combustion efficiency and gas concentrations, which were comparable to the experimental results. More recently, McIlveen-Wright, *et al.* (2006, 2007) investigated the co-combustion and co-gasification of coal, polyethylene waste and a range of biomass/biomass wastes with the aim of determining the most favourable operating conditions for each. The key finding was that for laboratory and pilot-scale fluidised-beds, co-firing 20 % biomass or plastic waste with coal had insignificant impacts on the efficiency, emissions, capital costs and the break-even point of the electricity selling price. Additionally, reusing the wastes results in benefits by disposing of them in an environmentally-responsible manner and there are also financial incentives for co-firing biomass and other wastes.

Fryda, *et al.* (2006) explored the co-firing of meat and bone meal with lignite, Columbian coal and olive bagasse, in terms of the emissions produced and the occurrence of bed agglomeration. As meat and bone meal is a volatile fuel, secondary air was required to minimise partial oxidation and reduce CO. Furthermore, other pollutants, such as NOx, were problematic as the fuel also had a high nitrogen content. The fuels did however have a low sulphur content, thus SOx emissions were minimal; the calcium-rich

ash therefore had little impact on further reducing these emissions. For the cases where the meat and bone meal were co-fired with the coal samples, agglomeration of the ash and bed occurred but were not problematic. Where co-firing occurred with the olive bagasse, severe agglomeration was noticed, leading to a dramatic loss of fluidisation; this was due to the presence of K and Si in the olive bagasse and chlorine and phosphorus in the meat and bone meal, coupled with the absence of inert clay minerals from the additions of coal, which were able to manage the moderate alkali ash content of the meat and bone meal. Cummins, *et al.* (2006) also studied meat and bone meal, with the aim of monitoring emissions and developing a dispersion model for its co-combustion with peat in a bubbling fluidised-bed. Based on the emissions, the dispersion of NO_2, SO_2, CO, HCl and particulates were examined for a proposed plant site, which were then compared to emission regulations at various scales. Gaseous emissions would comply with legislation to maintain high air quality standards, although particulate emissions would not and therefore control measures to reduce flyash release to acceptable levels would be required.

A similar investigation had previously been performed by Henihan, *et al.* (2003), looking at a dispersion model for emissions from a proposed site for the combustion of peat and poultry litter. Various combustion variables influenced both the combustion and emissions, SO_2 and NOx in particular; moreover, CO and VOC pollutants could be minimised by using optimum fluidising and secondary air, staging the secondary air or increasing turbulence. The dispersion model for this fuel also indicated that the emissions would comply with current legislation.

4.5.3 Emissions Control from Biomass Combustion in Fluidised-Beds

Following on from the above studies, many other investigations have focussed on categorising, measuring and/or minimising the pollutants emitted during the fluidised-bed combustion of various biomasses, particularly those which are co-fired. Several are based around computational modelling. Desroches-Ducarne, *et al.* (1998) examined the co-combustion of MSW and coal in a circulating fluidised-bed; the variation in NO, N_2O HCl, SO_2 and CO emissions for different fuel mixtures were characterised. As increasing proportions of MSW were added to the system, various alterations were noted: the form of nitrogen was modified (from N_2O to NO), SO_2 emissions decreased and HCl was more abundant due to the increased presence of Cl in the MSW. This Cl was thought to be significant in inhibiting oxidation, leading to a marked reduction in SO_2; CO concentrations were minimal with low levels of MSW, however with this lack of oxidising ability, increased CO and decreased CO_2 concentrations ensued. It was also seen that the combustion rate increased, due to higher percentages of volatile matter.

Another study in this area considered the trace element accumulation and release in the sand of a bubbling fluidised-bed, co-firing sawdust, peat and RDF (Kouvo and Backman, 2003). It was found that metals, such as lead, copper, zinc and manganese, were captured in the bed, but were released upon changes to the fuel characteristics or combustion conditions. Furthermore, it was discovered that the concentration of trace metal emissions did not necessarily correlate to the metal concentrations in the fuel, but they were

dependant on a complex process concerning: (i) the release of trace metals from the fuels used; (ii) the interaction between the fuel and the ash particles in the bed; and (iii) the release of the particles from the bed. This is primarily because the accumulation and release from the bed is due to the fuel characteristics, the combustion conditions and the degree of metal saturation of the bed. Additionally, Kouvo and Backman (2003) found that the bed particles became covered in a calcium- and potassium-rich layer, and at high temperatures, such as those used during fuel combustion, the layer may melt and play a significant role in the accumulation and/or release of the metals. They also utilised thermodynamic multi-phase, multi-component equilibrium calculations, the results of which suggested that Zn release from the bed was increased by the presence of Cl in the fuel, which converted the Zn to $ZnCl_2$ in the bed.

Çubuk and Heperkan (2004) completed both theoretical and experimental investigations into the formation of various pollutants during the combustion of sweet sorghum and Turkish lignites. Additions of the biomass reduced the concentrations of pollutants, such as SOx, compared to the combustion of the lignites alone. There were also opportunities to further minimise SO_2, NOx and CO emissions. By decreasing the overall ash content of the fuels, greater thermal efficiencies could be achieved. Elled, *et al.* (2006) considered the impacts of the presence of phosphorus on the capture of sulphur for the combustion of sewage sludge with wood or bark in a circulating fluidised-bed. Calcium improved sulphur capture, as the window for calcium sulphate formation was widened; when phosphorus was present in the system, however, when municipal sewage sludge was combusted, it interfered with this capture mechanism by binding itself to the calcium, which would otherwise be reacting with sulphur. Due to the competition between these, the phosphorus concentrations need to be taken into account when considering sulphur minimisation techniques.

4.5.4 Behaviour and Properties of Ash

Many studies have concentrated on the properties and behaviour of the ash produced from combustion, primarily as biomass fuels often contain a high percentage of ash. Zevenhoven-Onderwater, *et al.* (2000) used fuel analysis and advanced thermodynamic equilibrium calculations to predict the behaviour of ash during the combustion of various solid fuels. They found that the younger fuels, the forestry residue and the two willow samples (including soil contamination and no soil contamination) had fewer 'ash-forming' elements as included minerals, compared to the older fuels (peat and coal samples). In addition to this, the potential for slagging and fouling was predicted for each fuel, based on the results of the ash behaviour. Coal combustion should not result in any problems, although minor deposits may occur in the flue gas channelling with the peat sample when temperatures exceed 700 °C. This was also found to be true for the forest residue at 600-860 °C, and for the willow samples at temperatures of 840-1000 °C. Sintering was thought likely to occur for the soil-contaminated willow above 1300 °C.

Llorente and Cuadrado (2007) investigated how the distribution of inorganic elements in the ash from poplar combustion in a bubbling fluidised-bed was influenced by the amount of silica in the bed material.

It was discovered that the more silica present, the greater the retention times of specific elements. There was also much interaction between the ash and the sand bed, which impacted the distribution of the elements. In some cases, bed accumulation of particular elements, dependent on their volatility, was greater than 40 %, especially for Ca, K and other trace elements. If these did not accumulate in the bed, they were often emitted with the stack gases or deposited and sintered on heat exchangers within the system. A previous study by Llorente, *et al.* (2006) examined how limestone could be used to minimise or eliminate the agglomeration and sintering of ash from biomass (thistle and almond shells).

Öhman, *et al.* (2000) examined the characteristics of ash agglomeration during the combustion of various biomasses, including wood, bark, wheat straw, reed canary grass and RDF among others in a bench-scale fluidised-bed. The behaviour of the dominant ash-forming elements were analysed by collecting ash samples during controlled agglomeration tests, followed by scanning electron microscopy/energy-dispersive X-ray analysis to determine the agglomeration temperature. The particles in the bed were covered in a fairly uniform ash layer, containing primarily K_2O–CaO–SiO_2; S and Cl were found not to 'participate' in the agglomeration mechanism. The partial melting of the ash coating, mainly the silicate components, was thought to be the cause of agglomeration and defluidisation. Lastly, Rozainee, *et al.* (2008) considered the fluidising velocity during rice husk combustion and its effect on the carbon content of the ash. Fluidising velocities of 1.5-8 U_{mf} were investigated, where the optimum was 3.3 U_{mf}; this produced good sand bed-husk mixing, minimal sand being carried to the cyclone and a finer, low carbon ash (2 wt%). Greater U_{mf} values meant the husks were unable to penetrate the bed, leading to pyrolysis rather than combustion, resulting in higher carbon ash (4.5-6.6 wt%); the sand also elutriated and was collected in the cyclone. Lower U_{mf} values produced poor mixing, forming a stagnant rice husk layer.

4.6 SUMMARY

Fluidised-beds are a technology in which combustion and other thermal treatments can take place, of which there are several different designs. The main components were described in relation to bubbling and circulating fluidised-bed types. The principle that these reactors work on, fluidisation, was then explored, and the relative merits of these reactors were considered; the advantages of combustion in such a reactor include the generation of stable, uniform temperatures to minimise hot-/ cold- spots, which lessen specific pollutants. Fouling, corrosion and ash fusion are also less common. The main drawback is that the reactor has to be operated under the conditions where the bed is sufficiently fluidised. A number of factors concerning the fundamentals of fluidisation theory were also discussed, for which formulaic determinations were given where appropriate; equations for the pressure drop for example can be utilised subsequently for the system employed herein. In addition, the properties and classification of fluidised particles were considered, specifically focussing on Geldart's categorisation scheme. Examples of biomass combustion in fluidised-beds were also considered, comprising wastes and energy crops, where various studies investigated a range of aspects, including the emissions produced and the ash behaviour and properties, which can be compared to the data gained for SMC and coal tailings.

5

PELLETISATION THEORY

5.1 INTRODUCTION

This third theory chapter focuses on pelletisation, the process of 'size enlargement operations', by which solid particles are consolidated to form a more durable substance, with improved characteristics, such as increased density (Rumpf, 1962). Other words used for this include "tableting, compacting, extrusion . . . balling, sintering, nodulising, granulation and agglomeration", as well as briquetting, used specifically for describing the formation of coal briquettes (Messman, 1977, p1). Within this chapter, the main purpose for pelletisation is explained, with a focus on fuel, and the fundamental theory is discussed. The process of pellet formation is described, along with the types of pelletisers available and the technology used. Particle binding processes are obviously of utmost importance, therefore these mechanisms are also considered. The economics regarding pelletisation are assessed. Quality assessment methods are explored and thus the properties that make a good pellet can be identified. Lastly, the pelletisation of biomass, coal and coal tailings, and these substances combined is examined.

5.2 THE PURPOSE OF PELLETISATION

Pellets are formed when a systematic process consolidates loose particles using force; a great variety of technologies are available to perform this function, where the primary purpose is to form solid pellets of uniform properties and size (Rieschel, 1963). Lyne and Johnston (1981) consider five key purposes of pelletisation: (i) to prepare raw materials for further processing, as pelletisation is an excellent way to combine a number of initial materials or coarsen finer particles; (ii) to increase marketability as it can enhance certain properties, making a substance more attractive for a particular application, therefore the market value increases; (iii) to facilitate handling – some substances have undesirable properties, thus

pelletisation enhances their qualities, for example, making it easier to store, transport, handle and feed, due to the increased bulk density, which improves flow properties; (iv) to assist disposal – fine materials often require pelletisation so that the waste can be handled and disposed of safely without further processing; and (v) to recycle and/or reclaim materials – pelletisation, particularly of fine substances, can ensure they are suitable for other uses, or indeed be recycled back into the same process. Snow, *et al.* (1997) further discussed the aims of pelletisation; in addition to those above, a number of other reasons for pelletisation were suggested. There is increased control over the chemical and physical properties, particularly those enhanced by densification, such as solubility, heat and/or mass transfer, reactivity and size (Moore, 1965; Snow, *et al.*, 1997). Furthermore, forming coherent particles is an excellent way to alleviate dust-associated hazards and minimise caking (Moore, 1965). Li and Liu (2000) state that one of the main reasons for pelletising biomass for fuel applications is to increase its bulk and energy densities to be more comparable to coal, specifically when they are co-fired, facilitating fuel feeding. Thus this is the primary purpose of the intention to pelletise the SMC and coal tailings in this investigation, as both the bulk and energy densities are appreciably lower than for other fuel resources.

There are a number of advantages to pelletising fuel; there are also disadvantages, both of which are discussed by Holm, *et al.* (2006). The greater bulk density means less space is needed for storage and transportation costs are reduced. The moisture content is often lower or at least controlled to some extent, due to it being effectively 'squeezed out' during pelletisation, which improves the continuity of properties during storage. The higher energy densities of pelletised fuels directly improve the overall energy efficiency in a fluidised-bed, compared to unpelletised fuels. Combustion of pellets in this type of reactor is distinctly advantageous as this allows the fuel to burn in the bed due to the greater densities, meaning that the particles do not escape, unburned with the flue gases (Saenger, *et al.*, 2001). Problems associated with pelletisation include the power consumed during pellet formation and the technological issues associated with continuously producing a high quality, uniform product. It is obviously not beneficial to use more power and increase the cost of manufacturing pellets than what is gained through doing this. The rationale of pelletisation therefore is to produce a product with specific qualities, thus fulfilling one or more of the above purposes. Pelletisation, however, may not always be the solution; there are several prerequisites to ensure that pelletisation is suited to a specific application. Lyne and Johnston (1981) suggest that the material feed quality needs to be reliable, the particle size distribution appropriate, and, if necessary, a suitable binder included; further to this, it is vital that during processing, costs are minimised, while the quality of the product is kept constant and high.

5.3 PELLETISATION PROCESSES AND THEORY

The key variable in pelletisation is whether or not a binder is used; particle cohesion is increased beyond its normal level if a binder is included (Rieschel, 1963). In this type of pelletisation process, there are a number of stages in pellet production, discussed below, including pre- and post-treatments. In binder*less* pelletisation, the pressure used needs to be increased to much higher levels than where a binder is utilised,

to ensure satisfactory cohesion, as a binder is not present to perform this function; this binderless pelletisation will also be considered in a subsequent section. The sequence outlined herein for pelletisation is in fact similar for both binderless and binder-pelletisation.

5.3.1 Pre-Treatment

In both binder and binderless pelletisation, the material to be pelletised is often pre-treated in some way to enhance its properties and make production easier or less costly. Forms of pre-treatment may include manipulating the particle size distribution by crushing, grinding or granulation, and the material is often blended or mixed with the other materials that are to form the pellets (Snow, *et al.*, 1997). The final stage in pre-treatment, prior to forming the pellets, is to mix the particles with a suitable binder, if required. The binder and material should be thoroughly but carefully combined so that each particle is enclosed within a thin covering of the adhesive; this layer will be much thicker than the 'spheres of action' of the van der Waals' forces, thus the consolidation, and therefore the pressure required to achieve this, will be significantly lower (Rieschel, 1963). Excessive use of a binder is however both wasteful and costly.

5.3.2 Pelletisation: The Fundamentals

Pelletising, forming pellets from unconsolidated material is an essential part of many processes. There are various ways that it can be classified, discussed here, including the press process and pressure used. According to Rieschel (1963), pelletisation can be divided into the three methods of pressing (Table 5.1). As the press stamp goes into the die in Type 1, the stroke is constant; as the pressure is a function of the amount of material in the pelletiser – $f(Q_m)$, if there is not sufficient material, compression will not occur. Although the second type produces pellets of variable volume due to stoke variance, as the pressure is consistent, the quality is more uniform; this principle has aided the design of presses which operate using hydraulic pressure. Type 3 also produces pellets of consistent quality but differing volume; the constant stroke and pressure aid the formation of uniform pellets, upon which extrusion presses are based.

VARIABLE	TYPE 1	TYPE 2	TYPE 3
Stroke	constant	variable	constant
Volume	constant	variable	variable
Pressure	$f(Q_m)$	constant	constant

Table 5.1: The variable adjusted for the three different types of pressing processes.
Source: Rieschel (1963)

Another way pelletisation can be classified is by the pressure applied. There are three categories: low, medium and high pressure, as outlined in Table 5.2 (Rieschel, 1963). This pressure is used to densify material, and the higher the pressure, the greater the degree of densification due to volume and pore space reduction. Medium pressure is used for a range of organic and non-organic compounds, as well as soft metals, such as lead and copper; higher pressures are generally used for binderless pelletisation or where the substance is particularly hard or brittle, for example, sponge metals and inorganic compounds (Moore,

1965). If pelletisation is binderless, it is thought that pressure alone will be sufficient in forming a pellet strong enough for its subsequent use. If particle cohesion is not sufficient to form a coherent pellet, a binder is included, and once the pellets have been formed, any excess binder penetrates and fills pore spaces (Rieschel, 1963). A further classification is based on temperature, as elevating this may facilitate agglomeration, especially if a heat-softening binder has been applied or is inherent (Moore, 1965). Moreover, this is preferred for certain materials, particularly if a binder is not used; de-aeration and pre-agglomeration are used at temperatures up to and in excess of 1000 °C (Moore, 1965).

PRESSURE PRESS	PRESSURE RANGE	
	psi	MPa
Low	< 7000	< 48
Medium	8500-17000	58.5-117
High	23000-35500	158.5-245

Table 5.2: The pressure variations for pressing processes.
Source: Rieschel (1963)

5.3.3 Post-Production Treatment Processes, Storage and Transport

Pellets that are referred to as 'green' are ones that have only been pelletised, before any further processing has taken place. Pellets may be classified before or after treatment so inadequate ones can be recycled or rejected. Post-production procedures depend on the material pelletised and the end-use of the product; those that are employed include cooling, drying, curing, firing, sintering and/or carbonisation – the latter ones are often known as heat treating (Daubert, 1973; Messman, 1977). Drying or curing is common, especially if they are subsequently to be used in a thermal process, as this can improve the CV by eliminating moisture. The storage conditions are important and can severely affect pellet properties if not adequately managed. The temperature and ambient moisture are among a range of conditions that need to be regulated to avoid degradation. The pellet pile height also affects the final quality; it should be ensured that the ones at the bottom of the pile can withstand the weight of those on top. Additionally, the length of storage can affect pellet quality (Akgun, *et al.*, 1989). Following on from this, the transport conditions also require regulation, especially as vibrations and movement are among the main causes of pellet fracturing or disintegration. Pellets need to be strong enough to overcome these forces, although the travelling conditions can also be manipulated to ensure a better environment and fewer stresses.

5.3.4 By-Products of Pelletisation

By-products are common, but the substances produced vary with the material. The main classes of by-products are often the same, such as liquids that are forced out or effluent gases (Jones, 1969). The latter in particular require treatment to remove unwanted compounds before they are released to the atmosphere. Techniques have been introduced to deal with the by-products of pelletisation used in specific applications. In some cases, the by-products have their advantages and uses, although others do not and thus the processes used must minimise their impact or at least reduce the cost of their disposal. Some substances, particularly those from fuels, can be used to recover energy, which can then be

reintroduced back into part of the pelletisation process (Jones, 1969). Treatment processes are needed for other by-products so that the material can be recycled.

5.4 PELLETISER TYPES AND TECHNOLOGY

There are a variety of pelletisers that have been manufactured and developed over the years; each has a specific or range of specific applications, to which it is best-suited and the diversity of materials pelletised reflects this (Jones, 1969). The pelletiser chosen for a particular function is largely determined by the material properties (Rieschel, 1963). There are essentially two mechanisms: compression and extrusion. Here, pelletisation technologies shall be explored for both, although others will be briefly discussed.

5.4.1 Compression Methods

Compression or compaction utilises the mechanical consolidation of the constituent parts between plates containing moulds, through applying pressure (Daubert, 1973; Messman, 1977). Figure 5.1 outlines the three phases of the compacting sequence: charging, pressing and ejecting (Rieschel, 1963). During the first, the pelletiser and material are prepared, where the material is fed into the die. In the pressing phase, the material is compressed, thus a pellet is formed. Ejection, the final stage, is where the pellet is released from the mould so the process can start again. This method is utilised here in the experimental phase. A similar sequence is used for extrusion, except the material is extruded in the second phase. There are many variations of pelletiser that work on this principle; many subdivisions are reviewed herein.

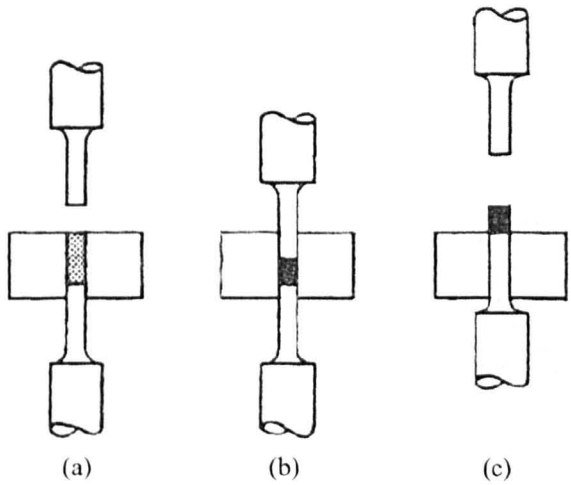


Figure 5.1: The three stages of the compacting sequence: (a) charging (b) pressing and (c) ejection.
Source: Daubert (1973)

Roll presses are an extremely common method of binder briquetting but have restricted applications for binderless pelletisation; consisting of two rollers that turn in opposite directions at a synchronous speed, the material-binder mix is fed through the gap between the plates and is compressed between them (Rieschel, 1963). Pellet quality can vary if the charge is not carefully controlled; adequate charge is needed to acquire a sufficient pressure to form good quality pellets, and this charge can be non-uniform in its distribution across the plates. If the centre of the plates acquires more charge than the edges, the

pressure can be insufficient to fully compact particles at the margins, resulting in inconsistent compaction and uneven pellet quality, which can give rise to cracks (Rieschel, 1963). A variety of types of roller presses are utilised. The double roll press (Figure 5.2) is a simple technique with many industrial applications due to its large capacity and ability to form pellets of various sizes; the shape and size of the mould is important and tessellating shapes means more pellets can be formed to make the process more economic (Jones, 1969). This press is also favourable as it has a low power consumption and can continuously produce uniform pellets, providing that the feedrate and bulk density remain constant (Jones, 1969). The entrainment, compression and release phases are the same as those described above; in the entrainment phase, the material is moved into the press and it is important that the correct amount is used to ensure the appropriate pressure is exerted to form optimum quality pellets. This depends on the dimensions of the rolls and their moulds, thus control of this is crucial (Jones, 1969).

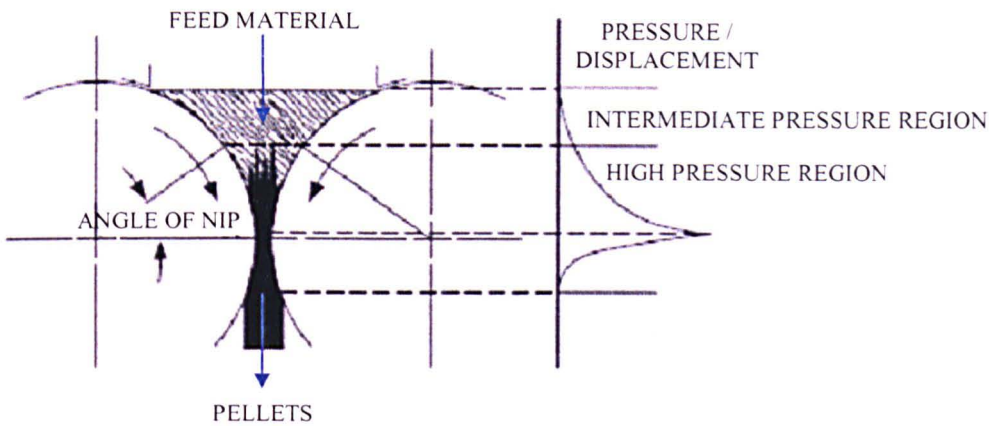
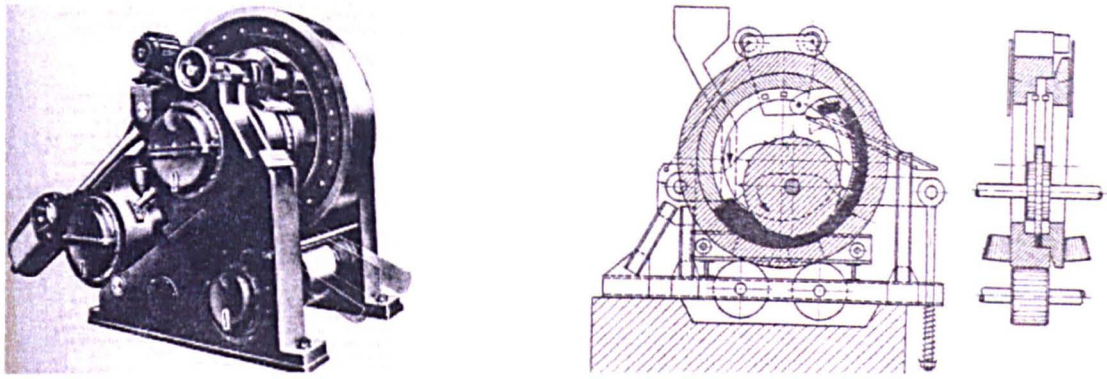


Figure 5.2: A schematic of the operations of a double roll press, showing the main compression areas. Source: Snow, *et al.* (1997)

The principle of operation during the compaction phase is that two cylinders of equal diameter are placed close together and rotate in opposite directions, with half the mould on each roll; the moulds match up and the material is compressed, forming a pellet (Jones, 1969). The rollers continue to turn and the pellet is released. The density throughout the pellet is not consistent, although this is more pronounced for larger pellets and so smaller ones are more uniform and hence better quality (Jones, 1969). Roller presses, such as those described above, are usually utilised under low pressure (see Table 5.2); a common use for these is the formation of char briquettes with a binder (Rieschel, 1963).

Ring roll presses (Figure 5.3) were developed due to the difficulties in pelletising hard materials. Operating on the principles of the Type 2 pressing process (see Table 5.1), the pressure remains constant (Rieschel, 1963; Jones, 1969). The mechanisms used to form pellets via this method are relatively straightforward; the press consists of a large ring with a series of moulds inside, where the press wheel rotates and compresses the feed material between them (Rieschel, 1963). There are many variations, as the basic technology has been developed and adjusted according to its needs. This is based on the properties of the material, namely forming uniform pellets of hard or dusty material. Varieties include two-strand presses, horizontal pressing rings with two wheels and split/closed moulding tools (Rieschel,

1963). This type of roll press can work under extreme conditions, such as very high pressures in a continuous operation (Rieschel, 1963). Ring roll presses are advantageous as they do not consume large amounts of power and have a high capacity. Pellet size and shape, however, are not always uniform. The main difference between the types of presses is the way in which pellets are released (Jones, 1969).



(a) (b)

Figure 5.3: (a) A ring roll press and (b) a ring roll press of Apfelbeck design for char briquetting. Source: Jones (1969)

5.4.2 Extrusion Methods

Extrusion methods, in contrast to compression, press the substance through an orifice to form pellets (Messman, 1977); examples explored here include screw or piston extruders, table presses and pellet mills. Extrusion presses, comprising a drive mechanism and press head, operate in a similar fashion to piston-type engines, where the piston forces the material into the mould and partially compresses it, before pushing it through an orifice. Once as many pellets have been produced with the material in the mould, the piston is removed so more material can be added (Rieschel, 1963). This forms good quality pellets under carefully controlled conditions, using constant, medium pressure, where pellet size is altered by changing the material density (Jones, 1969). For extrusion pelletisers, the first part of the mould is slightly convergent, to aid the partial compression of the material, and the second part is divergent, which is set to be consistent with pellet expansion, to avoid cracking and damage (Rieschel, 1963). It is however expensive to manufacture small pellets using this technology and is therefore only economically-viable to make larger ones (Jones, 1969). The cost is also increased by the high power utilization. The quality of pellets formed is strictly dependent on the pressing period (Rieschel, 1963). Several materials, including many types of biomass, as well as a range of coal-based fuels are pelletised using this technology; char, for example, can be briquetted like this without the need for a binder (Jones, 1969).

Screw or piston extruders push material through orifices to form pellets (Figure 5.4). This technology is not new, thus much development has occurred (Schweizer, 1963). One such example of this development is the co-rotating twin screw extruder, consisting of a feeder with an adjustable feedrate and a series of screws to move the material towards two orifices (Schmidt and Kleinebudde, 1998). A liquid pump is also attached to obtain the optimum material moisture content; this is necessary as the moisture in the extrudate, and hence pellet quality, depends on the material feedrate and the liquid input (Kleinebudde

and Lindner, 1993; Schmidt and Kleinebudde, 1998). It is vital that when this occurs, the container is not full so optimum screw speeds and material flowrates are achieved, as the process becomes somewhat different if this barrel is full. The most influential factors on pellet quality are the screw speed, feedrate, temperature and pressure, although the moisture content is the most dominant variable (Kleinebudde and Lindner, 1993). Screw extruders are mainly used for pelletising plastic materials, though Schweizer (1963) discusses the extrusion of materials lacking ideal properties. Due to advances in this process, the usually difficult pelletisation of these substances is no longer an issue. Additive development has further aided the use of this technology, as these produce more suitable flow properties and can act as a binder. Another factor to affect agglomeration of such materials is the grain size distribution, which determines flow. Further to this, Schweizer (1963) considers the advantages of screw extruders, including low initial investment and maintenance costs, high production rates, the ease of altering pellet dimensions and the fact that conditioning and pelletisation occur in a single unit. Although 'unsuitable' substances are pelletised in this way, most parts that degrade are easily replaced.

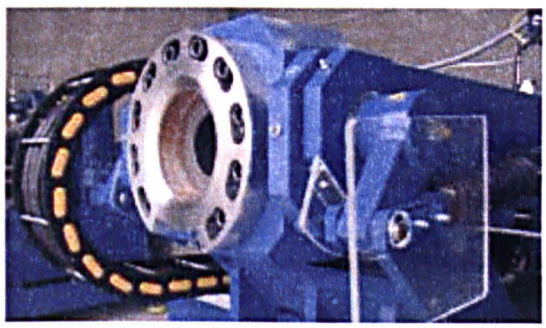


Figure 5.4: A piston extruder – a pelletiser that uses the extrusion principle.
Source: LOOMIS Products (n.d.)

There are two distinct types of table press: the rotary or rotating table press and the sliding table press, which are the oldest type of pelletiser and normally operate under low pressure (Rieschel, 1963). The key difference in the operation of these presses is that the number of strokes differs greatly per hour, and therefore so does the pellet output; this is primarily because the three stages of pelletisation (charging, pressing and ejecting) occur concurrently for the rotary press, whereas these functions are performed sequentially in the sliding table press (Rieschel, 1963). During the operation of the latter, the table slides back and forth instead of rotating, like in the rotary press. The rotary table press generally produces large pellets but are for the most part no longer used (Jones, 1969). Their simple design was subsequently developed however to incorporate hydraulic operations to manufacture smaller pellets more suitable for fuel applications. Rotary table presses have various designs dependent on their operation. The variations for simple table presses, for example, include horizontal or vertical component operations (Jones, 1969).

Pellet mills are in fact quite similar to ring roll presses, described above, except they use extrusion rather than compression. The main elements of this type of technology are shown in Figure 5.5. As with a ring roll press, the material is contained in the centre of the ring and pellets are formed at the periphery; in this case, they leave the ring after pelletisation. Pellet mills normally have a conditioning chamber, where the

material is mixed and conditioned with steam or dry lubricant to aid pelletisation. The material is fed into the centre of the pelletiser by gravity, and is then forced out through a series of orifices (Robinson, 1971). Although this is a continuous process, where the material is fed into the main chamber without the need for the roller to be stopped, batches are often made. The design of the apparatus is such that when the pellets have reached sufficient length, they touch the cutter and pellets are formed. Figure 5.5 shows a design with only one roller, whereas many modern designs have at least 2, as seen in Figure 5.6.

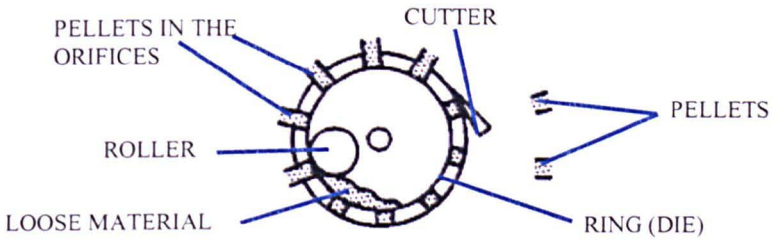


Figure 5.5: A schematic of the operating principle of a pellet mill.
Source: Snow, *et al.* (1997)

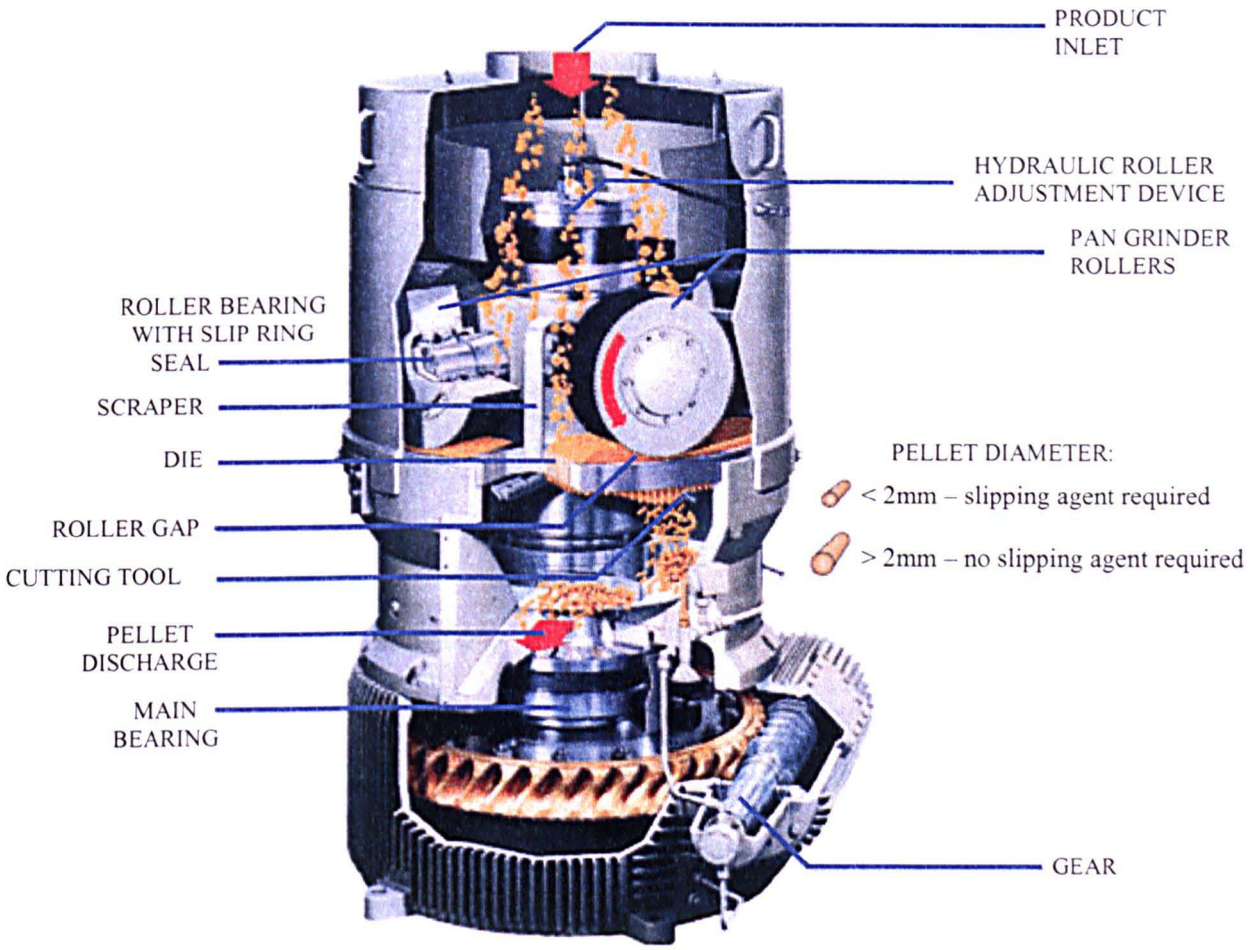


Figure 5.6: A Kahl pellet mill – based on the design of Amandus Kahl's flat die pellet mill.
Source: LCI Corporation (n.d.)

The ends of the pellets can be rough, whereas for compression, pellets have flat surfaces. Due to this cutting, pellet size is not necessarily uniform, particularly if there are variations in material properties, such as density. Altering the die speed can also modify pellet size and is one of the variables manipulated

to form pellets of optimum quality (Robinson, 1971). This speed also varies with material properties; low revolutions for heat sensitive or large-section pellets and high speeds for materials with exceptionally low bulk densities; medium speeds are a compromise, so a variety of substances with differential properties can be pelletised into different sized pellets. Pellet mills are constructed so more than one rotation speed can be achieved, thus the equipment is flexible and can handle a variety of materials (Robinson, 1971).

5.4.3 Other Methods

Although extrusion and compression are by far the most common techniques, a number of other methods are used to pelletise materials, including sintering, mixing, drying and tumbling (Lyne and Johnston, 1981). Table 5.3 outlines the pelletiser types associated with each mechanism, however the first three are rarely used commercially. The tumbling principle is the most often employed, and is the one that also determines the functionality of tumbling drums, categorised on the angle of inclination (Lyne and Johnston, 1981). The basic design of a horizontal drum pelletiser contains baffles to control growth, lifters to aid tumbling and have length-to-diameter ratios of 2:1 to 4:1. More complex designs distinguish between pellets that are over-/under-sized, crushing larger ones and recirculating those that require further enlargement (Lyne and Johnston, 1981). The drum in this case is horizontal, whereas in inclined pelletisers, the axis is at an angle, between 45° and 55° for disc pelletisers, but less for drum pelletisers, typically 20-35° (Figure 5.7).

PELLETISATION MECHANISM	PELLETISER TYPES
Sintering	rotary kiln shaft kiln
Mixing	spiral path granulator ribbon blender granulating mixers
Drying	spray dryer band dryer for preformed paste instantisers fluidised-bed granulator
Tumbling	drum granulator inclined disc/drum pelletiser

Table 5.3: Table outlining the different types of pelletiser available for the different mechanisms. Source: Lyne and Johnston (1981)

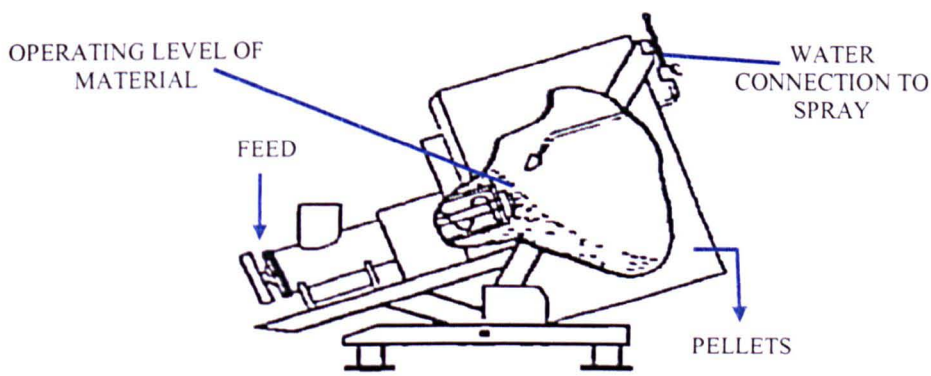


Figure 5.7: A schematic of an inclined drum pelletiser. Source: Lyne and Johnston (1981)

5.5 PARTICLE BINDING THEORY

5.5.1 How Particles Cohere During Pelletisation

There are many phenomena thought to influence the way in which particles are able to cohere during pelletisation. A number of aspects that have been deemed particularly significant are examined here; these include surface tension, capillary forces, inter-locking, liquid bridging, friction, van der Waals' forces, solid bridges, electrostatic interactions, compaction, shape phenomenon and material-specific forces. Rumpf (1962) and Jones (1969) discuss these in depth, the latter with reference to coal and char.

It is theorised that there are many different types of adhesion that influence the agglomeration of particles during pelletisation. Surface tension and capillary forces are related influences on particle adhesion, both of which are suppositions related to the inherent moisture content of a material. If there is enough moisture to coat each particle at the maximum pressure achieved during pelletisation, the forces at the surface – the surface tension – can bind particles to one another (Jones, 1969). For this process to work effectively, however, the optimum moisture must be acquired and used for the specific substance. It has been reported though that this, as with particle interlocking, may in fact make a fairly insignificant contribution to overall agglomeration. Capillary forces aid liquid bridging between particles and can also promote binding due to surface tension; if the voids between particles are partially or fully filled with liquid, known as pendular and capillary state respectively, liquid bridging and interfacial forces exist (Rumpf, 1962). If too much liquid is present and the solid is entirely encased by it, however, this considerably reduces capillary forces. Moreover, the friction generated during pelletisation concerns moisture at the surface, aiding the stickiness of particles; for this friction to impact adhesion, the particle surfaces need to be extremely close, usually a matter of Angstroms (Jones, 1969). Conversely, these forces acting on the particles may be van der Waals' forces – temporary induced dipole interactions – and may simply be able to overcome any forces opposite to adhesion (Jones, 1969). Whilst these are of particularly small range, if particles are very close together, they can aid binding (Rumpf, 1962). Solid bridge formation, as opposed to liquid bridging, can be initiated between particles by four mechanisms (Rumpf, 1962): sintering, crystallisation of dissolved materials, hardening of binding agents and melting.

Whilst many of these phenomena are thought to significantly contribute to particle binding, the influence of interlocking may assist particle binding, but is generally regarded as less important for most substances. Particle interlocking could occur due to the elasticity of the particles, which hold them in place (Jones, 1969). This may be of particular relevance when the particles in the pellets are not uniformly shaped, although it is generally thought to have little effect. Another factor also thought to be fairly insignificant is electrostatic forces. Due to friction, particle charging may occur, although charge equalisation occurs to repeal this effect (Rumpf, 1962).

The compaction of the material, even in extrusion processes, is another aid to agglomeration. The initial compression is a balance between the particles resistance to deformation and the pressure exerted,

although particle friction is also a factor. As pressure increases, the resistive forces are less influential and the void spaces between particles are reduced, thus particles agglomerate (Jones, 1969). If pressure is further increased, larger particles may disintegrate and eventually elastic and plastic deformation occurs; if pressure is then released, some elastic recovery of the material may take place (Jones, 1969). If the pressure continues to rise again, the pellet gradually becomes stronger and the density increases.

The 'shape' phenomenon is another factor influencing agglomeration, particularly for extrusion methods. Described by Jones (1969), this is where a material undergoing pelletisation is subjected to a shear strain, thus the density can be increased and the elastic recovery decreased. This is able to minimise the void space by compression and increase surface contact by the strain, but this effect is known to vary from material to material and is quite insignificant for those with little elasticity. Consequently, semi-plastic materials, such as coal, are ideally suited to this form of agglomeration.

Lastly, material-specific forces, such as tar binding, are another adhesion-related factor, which influences agglomeration. For tar binding, tar is released when coal is heated to coat particles, effectively acting as a binder. The relationship between the amount of tar and the strength of coal briquettes is clear (Jones, 1969). Although there is a distinct correlation between these, if the amount of tar increases beyond threshold levels, briquette strength decreases, thus an optimum amount of binder should be established.

5.5.2 Factors Affecting Binding Strength

The various phenomena and properties described both above and throughout this section relate to those of the material that affect binding strength; of course, pelletisation conditions also appreciably impact binding, which is considered in detail in a subsequent section. The first factor to influence binding is the particle size and its distribution. The sizes of the particles in the material can affect the strength of the binding, as primarily this alters the distance that the compression surfaces have to travel (Jones, 1969). In some cases, particle size is most important when choosing a pelletiser. This does not appear to be an issue for some types, such as ring-roll presses, which simply adjust the length of the pellet with this, but for others, the impact is evident. Double roll and rotary table presses require some form of control over either the material feedrate or bulk density if particle size varies notably (Jones, 1969). The particle size distribution in the initial stage of compaction, where void space is minimized, is thought to be more influential than actual particle size (Jones, 1969). As the degree of compaction is dependent on void spaces, which in turn is determined by the particle size distribution, it is vital that this is known to ensure optimal pressure is applied and therefore sufficient compaction is attained. Particle sizes between samples can vary widely, though their void spaces can be similar (Jones, 1969). As discussed earlier when considering binder application and pre-treatments, each particle needs to be evenly covered with a thin film of adhesive, regardless of size; this layer will usually be thicker than the 'spheres of action' of the van der Waals' forces, thus the consolidation and pressure required to achieve this will be significantly lower (Rieschel, 1963).

The second factor is the material composition; this may include the moisture, mineral and volatile matter content. As discussed above, moisture is key to ensuring the adhesion mechanisms function adequately. The moisture needs to be optimal, not too high or low, otherwise the binding properties of the material can be disturbed. This is why the moisture content is often manipulated or controlled in some way, so that ideal pelletisation can occur. If the materials are too wet, this can prevent sufficient compaction, whereas if the material is too dry, this can cause elevated friction between the material and the mould, effectively 'polishing' the surface of the pellet and thus wasting energy. Although the inherent moisture within a material and the moisture added or removed, through liquid additions or drying techniques, are the most obvious sources of moisture, the ambient moisture in the air can also affect the moisture content of the pellets. If the air is very moist, due to precipitation, dry materials are able to absorb some of this moisture; additionally, this moisture in the air prevents the natural drying of the material and pellets. The opposite of this is also true, where very low air moisture can promote drying, and dry materials beyond their ideal levels. The composition of the remaining material also affects binding, particularly the mineral and volatile matter. The clay mineral content, for example, can be assessed by XRD (x-ray diffraction). Burchill, *et al.* (1994) found that mineral inclusions were where fractures and cracking originated in pellets. These minerals, moisture and volatile matter are of particular importance if the material is to be used as a fuel and it is necessary that these components are evenly distributed (Berkowitz, 1979).

A number of other influences may affect agglomeration, most of which are specific to a particular material. Coal was used as an example above, as when heated, it essentially forms its own binder to aid agglomeration. It is necessary to determine these properties for individual substances through assessing and quantifying the affect they have on the overall binding.

5.5.3 Elasticity and Plasticity

Different materials have varying properties and thus the elasticity and plasticity also differ; these properties in turn affect the characteristics of the pellets formed (Jones, 1969). Plasticity is the ability to be moulded and when pressure is applied, the material can be permanently deformed. It has been found that as plasticity increases, the strength of pellets is enhanced due to the increase in the particle surface area and the decrease in void space upon their deformation; using pelletisation conditions that alter this property, such as elevated temperatures, can significantly modify pellet strength (Jones, 1969). Plasticity is therefore regarded as one of the most predominant factors affecting the pellet strength (Jones, 1969).

Elasticity is another property and although similar to plasticity, it is distinctly different. While plastic substances can be permanently altered, elastic materials recover their original shape once the force that caused the initial deformation is removed; it is thus most apparent in the final stages of pelletisation (Jones, 1969). Some materials exhibit one or neither of these properties, whereas coal and other solids appear to have some degree of both. It has been found that materials with high elastic recoverability also have more faults; due to this, it is thought that the elasticity of a material does not enhance its pelletisation

potential, as opposed to plasticity, which does, and therefore testing has been conducted on materials and pelletisation techniques to remediate this effect (Jones, 1969). The results include tapering the mould, which allows for the gradual expansion of pellets on their release, to minimise the risk of faults and cracks. Lateral strain is steadily released, as abrupt releases of pressure cause faulting (Jones, 1969).

5.5.4 Choice and Application of Binders

In the above discussion of the cohesion mechanisms that occur during pelletisation, the processes that were considered are the ones which occur naturally between the particles in a material, and the effects of binders are not considered. The influence of a binder on agglomeration, however, is often significant, and is required to be so; the function of a binder is to enhance the agglomeration properties of the substance, through increasing or promoting one or more of the specific aspects above. Binders are added to the material requiring pelletisation for the purpose of reducing the adversity of pelletisation conditions that would otherwise be needed. This includes reducing the temperature and/or pressure necessary to form pellets of sufficient quality. The proportion of binder used depends on the materials' properties and can vary from less than 1 wt% to more than 30 wt%, (Messman, 1977). The choice of an appropriate binder is vital for cohesion to occur the way it ought; trial-and-error is unfortunately the best method of finding a suitable binder that both performs the function adequately and produces a useable and desirable product (Messman, 1977). There are, however, a number of other issues that need consideration before a binder is used. Cost is always highly influential; not only does the binder need to be cheap and readily available, but it also needs to be used sparingly, so that even cheap binders do not cause excessive cost.

There are a number of factors that should be considered when applying a binder. Messman (1977) outlines that the particle size, temperature, pH and the mixing of the material and binder are imperative to the formation of coherent, homogenous pellets. The particle size and the particle size distribution can influence the effectiveness of the binder and these can be manipulated to control pellet properties. The density and durability can be managed and the amount of binder used can be minimised. An optimum temperature can often be established so that the binder works and performs its function to the best of its ability, as many can be temperature-sensitive. This is particularly integral if the binder is organic or expensive; temperatures that are either much higher or lower than the range the binder can withstand may result in poor mixing, sorption of the binder or changes to the binder function or the material. Utilising the most favourable pH, specifically when using water-soluble or emulsified binders, can also be beneficial. Mixing the material and binder can effect the final product in several ways; not only will thorough mixing enhance pellet quality and be economic in terms of binder use, but the mixer used and mixing rate utilised may also impact the pellets.

5.5.5 Review of Commercially-Available Types of Binder

There are many types of binder available to perform the above described function; many are used on a wide scale, while others have highly specific applications. They are normally classified into groups,

although there are a number of different methods depending on the factors considered. Messman (1977), for example, categorises them according to their function, as follows:

- matrix-type binders – a continuous matrix is formed, within which individual particles become completely surrounded.
- film-type binders – usually in the form of a solvent, which coats the particles.
- chemical-type binders – take part in reactions, either with itself or with the material.
- lubricant-type binders – minimises the interparticulate friction and can be used with a variety of other binders.
- combination binders – binding agents that perform more than one of the above functions.

Water, in fact, is one of the most practical binders available, which also acts as a lubricant, thus experimentally determining the most appropriate moisture content for pelletisation is often essential. The advantages of this are that it is cheap, freely available and safe, and therefore can be applied to many materials (Moore, 1965). Other binders that are often used include sugars, starch, soluble salts combined with a solvent, tar, oil, waste liquors and various alcohols. Many of these are known as heat-softening binders, which work more effectively when the temperature is raised to moderate levels (Moore, 1965). Some materials do not require the addition of a binder as there is already a substance inherently present within them to act as this binder. The example of coal and tar-binding was described above. There is a similar process that occurs for certain biomasses; on heating, lignin and often cellulose softens and aids the agglomeration of biomass particles. This fills in void spaces and solidifies again on cooling to form strong pellets (Gilbert, *et al.*, 2009). Coupling agents are another sort of material that can improve particle bonding; in some cases they simply enhance it, while in others they initiate the bonding. This can be done, for example, using hydrophilic particles and a hydrophobic binder (Messman, 1977).

One last point to make on this topic is the inadvertent impacts binders sometimes have. While a specific binder may enhance agglomeration, it may have other effects on pellet properties. One such example is artificial logs used in log-burning fires, which are often a combination of crude petroleum wax and sawdust, where the wax acts as both a binder and a secondary fuel (Messman, 1977). Sometimes these unintended effects are not beneficial and may have severe limitations on the properties and/or uses of the pellets; they may degrade the pellet in some way, make them more vulnerable to biological decay, especially if an organic solvent is used, or may produce additional and/or more toxic pollutants if they are used as a fuel, which can be degrading to both the environment and the equipment employed.

5.5.6 What Happens if a Binder is Not Used?

According to Messman (1977), even if a binder is not used, any solid substance can be pelletised, in theory, providing enough force is used to compact or extrude the material. The cohesion of particles in binderless pellets originates from the formation of relatively large surface areas provided by their compaction and thus also through the minimisation of void space. Some substances are, however,

particularly difficult to pelletise without a binder, especially if they are rigid; determining the optimum particle size is usually beneficial in these circumstances (Messman, 1977). When a binder is not included, cohesion is affected by the van der Waals' forces which bind the particle surfaces; high pressures, much greater than in binder pelletisation are needed to achieve this (Rieschel, 1963). Where the surface area is large (fine material), the pellets are generally stronger. The particle size distribution is thus an important factor in cohesion, as these forces need to be evenly distributed to ensure uniform strength and quality (Rieschel, 1963). Much experimentation on binderless and binder pelletisation has been performed. Beker (1997), for example, formed briquettes with and without a binder to compare the effect on their properties and Beker and Küçükbayrak (1996) investigated the effect of altering the amount of binder used in the briquetting process. Akgun, *et al.* (1989) found that for fragile Turkish lignite, a binder was necessary for pellet quality to be adequate. As stressed previously, these factors have to be established for individual substances.

5.6 PELLETISATION ECONOMICS

The cost of pelletising a material can vary widely, from a few pence to several pounds per tonne (Moore, 1965). If the material is easy to pelletise, these costs are often low, but as the process becomes more difficult and complex, pelletisation is more expensive. The overall cost is dependent upon a range of factors, which vary considerably with the material and machine. The main costs of the pelletisation process have been divided into six main areas: (i) the costs of the material (and binder, if used), (ii) the initial costs of the pelletiser, (iii) expenditure for the running and maintenance of the pelletiser, (iv) the costs of any treatments, (v) the transport and storage expenses and lastly (vi) dealing with any waste.

The first of these is the cost of the material to be pelletised and whether a binder is needed to achieve this satisfactorily. The material usually incurs a certain degree of expenditure, unless it is a waste for disposal that is to be agglomerated. Binderless pelletisation is obviously cheaper in terms of the expenditure for a binder, which is eliminated. The additional pressure needed to form pellets of sufficient quality, however, may negate this; if greater pressures are required to form pellets of adequate quality, the operations are significantly more expensive (Moore, 1965). Furthermore, there is little market value for less-than-optimal pellets and the extra expense of using a binder will no doubt be of benefit later in terms of pellet quality. Although the cost of binders vary greatly, they can be expensive, which is why their economic use is vital (Moore, 1965); not only in terms of the cost but also in terms of their impact on pellet quality.

The second factor is the initial cost of the pelletiser. The pelletiser chosen depends on the material properties as well as the volume of pellets to be produced, and the costs of these can vary significantly. Thirdly, the running and maintenance costs also require consideration. The energy consumption of the pelletiser during operation results in another incurred cost (Jones, 1969); if extreme pelletisation conditions, such as high pressure or temperature, are required, the general running costs can be vast. Other inputs, for example any liquids or binders, also incur further expense. Maintenance costs also vary,

but can be especially high if abrasive or corrosive materials are used; this degrades the mechanisms of the pelletiser which subsequently need replacing. The pre- and post-treatment techniques used also increase the costs of pellet formation. Pre-treatments are often required, usually to control the moisture content, to make the material more suitable for pelletising. This again increases in the overall energy consumption of the process and can often be more expensive than pelletisation itself (Moore, 1965). A number of other processes may be required depending on the properties of the initial material and the final quality of the pellets. Pelletising material with optimal inherent moisture and with no post-treatment is relatively cheap, although does not necessarily form the best quality pellets (Moore, 1965).

Many materials produce wastes or by-products; some can be recycled to the process, used for energy recovery, or even sold as products themselves, which can thus enhance the economics of the procedure by bringing in additional revenue. When dealing with unwanted by-products, their treatment and disposal are unfortunately often costly. Transportation and storage of the pellets and their by-products are further costs usually incurred by the manufacturer, although this is often taken into account in the final price of the product. The distance travelled can be the difference between profit and loss. Employing the optimum conditions in both of these processes is also necessary and therefore increases the costs further.

5.7 METHODS FOR QUALITY ASSESSMENT

Product characterisation is important in assessing the quality and properties of pellets – it is also a method for quality control, although suggestions are not made for altering the process (Snow, *et al.*, 1997). Pellets need to be assessed and evaluated on their physical and chemical properties to ensure they suit their purpose. The physical properties comprise pellet size, particle size distribution, strength, durability, density and porosity. Although there are often standardised methods to quantify these for materials, there are rarely established standards for pellets, although this is being addressed (Obernberger and Thek, 2004); sometimes, there may be more than one recognised standard. Quality assessment methods of the pellets made in this investigation will therefore be based on the methods explained in this chapter. The methods described herein therefore are common techniques, but not necessarily the standard used to test all pellets. Pellet quality is likely to be significantly affected by the properties of the original materials, as well as by the pelletiser used and the conditions under which it was operated. The analysis of the chemical characteristics of pellets, including the composition of the various components, is therefore also important (Snow, *et al.*, 1997; Holm, *et al.*, 2006). Methods for these will be described in a subsequent chapter of this study. From a discussion of these, optimum pellet parameters can be defined.

5.7.1 Pellet Size and Particle Size Distribution

The mean pellet size is the average size of the pellets produced and this can be attained simply by measuring the dimensions of a number of pellets and forming a mean of the height, width and depth, or diameter if they are cylindrical. The sizes of pellets formed are not necessarily uniform and thus the range of pellet sizes is useful information to have, particularly regarding their handling.

The materials' particle size distribution is also significant in determining pellet quality; it is therefore often necessary to establish this, upon which inferences concerning agglomeration can be based. This may also be one of the influential factors that determines whether or not a binder is needed. This can be done in a variety of ways; the first method involves scanning electron microscopy, which can also identify particle bonding mechanisms. Alternatively, this can be done by passing the sample through sieves of decreasing size. If the particle sizes are particularly large, they could even be measured by hand. These are all standard methods, not only for applications to pelleted material.

5.7.2 Compressive/Tensile Strength and Hardness Tests

The compressive or tensile strength and hardness of pellets are intimately related. Compressive strength is an important factor to investigate as it is the force the pellet can endure and is an indicator of cohesion. This force can be indicial of the maximum height of a pellet pile that the ones at the bottom can withstand, which expresses vital information concerning the storage and transportation of pellets. This can be assessed using a tensometer and converted to the tensile strength, which is connected to pellet dimensions and shape. This strength is the maximum force exerted before the pellet deforms, cracks or breaks (fracturing). When this is tested, the fracture in the pellet is not likely to be ideal, but will be determined by the particles' surface within the pellet, as seen in Figure 5.8 (Rumpf, 1962). Hardness tests, by comparison, examine the friability of pellets; friable materials form pellets that can deteriorate rapidly during transport, storage and handling by pressure, vibrations, abrasion and impacts. It is therefore necessary to assess this property and ensure hardness is sufficient for the use which they are intended. Tests of this nature include the evaluation of the pellets' ability to endure these forces, thus investigates similar qualities as durability testing below (Jones, 1969).

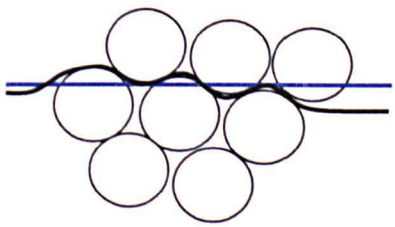


Figure 5.8: The lines of ideal fracture (blue) and actual fracture (black) during compressive strength testing. Adapted from: Rumpf (1962)

5.7.3 Mechanical Durability and Shatter Index

Pellet durability is another factor indicating pellet quality, as it can contribute information leading to the determination of appropriate transport and handling conditions (Temmerman, *et al.*, 2006). There are several ways in which this important quality indicator for fuels can be determined; despite this, there still is no entirely standardised method. There are two main techniques, depending on the empirical method used; a drum or tumbling device to test the breakage of pellets by both impact and abrasion is the most common (Patrick and Wilkinson, 1978). Alternatively, a vibration method can be used, whereby pellets are placed on a tray that vibrates at a calibrated frequency. In both instances, it is important to record the size and/or weight of the pellets so it can be associated to the amount of breakage. Patrick and Wilkinson

(1978) suggest a number of parameters that need consideration when such methods are employed: drum dimensions, lifting flights, rotation and moisture.

Temmerman, *et al.* (2004; 2006) aimed to add some degree of standardisation to the mechanical durability testing of solid biofuel pellets and briquettes. Defining durability as a pellets' resistance to shocks and friction by remaining intact, they suggest standard methods and procedures for both pellets and briquettes, through examining 5 biomass briquette types and 2 pellet selections (15 biomass pellets types for selection 1, and 11 for selection 2); the biomasses included mixed wood, softwood, hardwood and agricultural residues, such as straw. The moisture content was limited to a maximum of 10 %, as Obernberger and Thek (2004) demonstrated there was no relationship between moisture content and mechanical durability after moisture drops below 10 %; thus this would not impact upon the results. From comparing the outcome for four techniques, the following methods were outlined for pellets and briquettes respectively, as they gave the most repeatable and reproducible data.

For pellets, using an ASAE S269.4 DEC 96 tumbling device (Figure 5.9) gave the best results. The aluminium or stainless steel boxes were 300 x 300 x 125 mm and rotated at 50 rpm on their central axes, with a 230 x 50 mm baffle. Furthermore, sieving took place to remove fine particles (< 3.15 mm) and durability was expressed as a percentage of the initial weight, usually 500 g, after 500 rotations. Though an accuracy level of 0.5 % could be achieved, the variability of materials was found to influence this, particularly the fuel type and properties; pellets with high durability had the least variation in their results. In order to achieve this degree of accuracy, this method required a minimum of three replications.

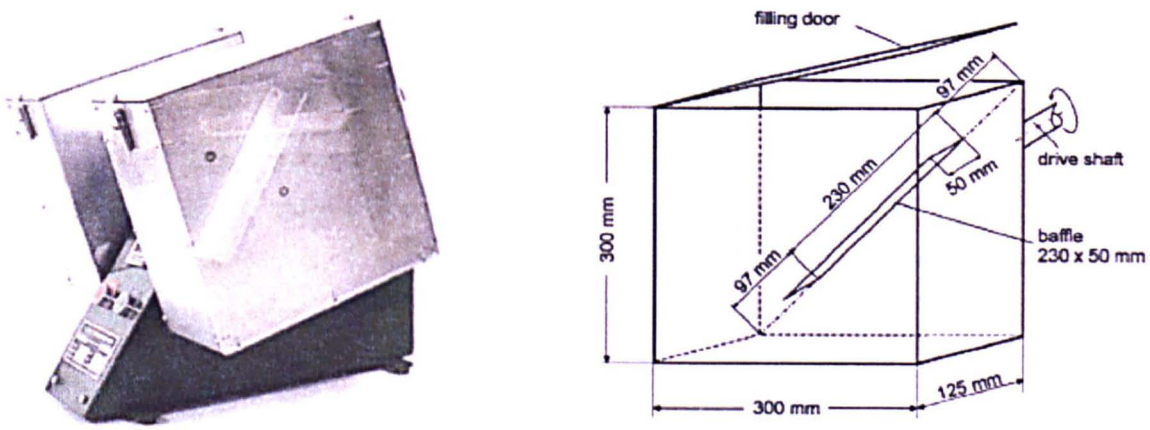


Figure 5.9: The ASAE S269.4 DEC 96 tumbling device for pellet durability testing.
Sources: Temmerman, *et al.* (2004; 2006)

The test method for briquettes, however, was somewhat different and used a dustproof cylindrical drum with a perpendicular baffle (Figure 5.10) to produce good, yet variable results. This drum had a capacity of around 160 l and rotated at approximately 21 rpm. The conditions under which this was used to attain the most reproducible results were 2 l of briquettes and 105 rotations, after which a durability index was calculated, based on the material left after sieving at ⅔ of the briquette diameter, expressed as a percentage of the initial mass. There was moderately high variation when the complete dataset was taken

into account and five replications were thus recommended. The problem with both these methods, however, is that the differences between pellets and briquettes are not described and thus the appropriate use of each is unclear. From the pictures therein, the distinction may concern size classifications, where briquettes appear considerably larger, approximately 5 cm in diameter and 10-15 cm in length, whereas pellets were smaller, 2-5 cm in length and less than 1 cm in diameter (Temmerman, *et al.*, 2004).

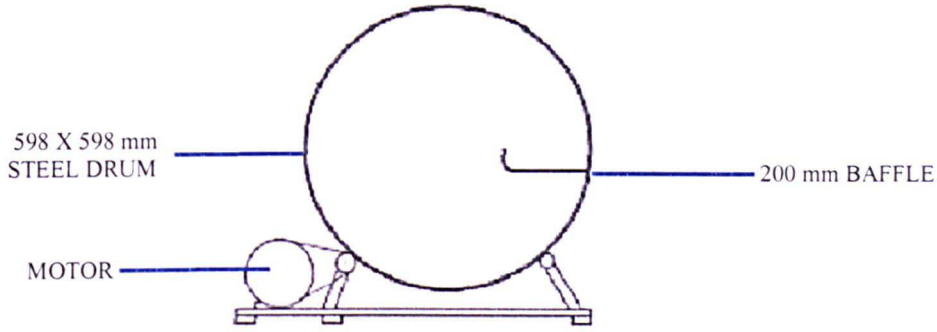


Figure 5.10: Schematic of the durability drum with a baffle for briquettes.
Source: Temmerman, *et al.* (2004)

The shatter index is the second test for mechanical properties; this is different from durability and is evaluated simply by an impact (Patrick and Wilkinson, 1978). There are many standards for performing this test on coal; Patrick and Wilkinson (1978) identify and describe the ISO Standard 616, ASTM Standard D 3038-72 and the British Standard 1016, Part 13.3. A known amount of sample, usually 25 kg, is amalgamated so that the test sample above a minimum size has the same proportions as the main sample. The next stage is 'impact breakage', where the pellet is dropped from a height of 1.83 m four times; the shatter index is subsequently given as a weight percentage of the remains above a certain size.

5.7.4 Density and Porosity

The density and bulk density are important pellet parameters to determine, as they are a direct indication of quality and can affect combustion properties, among other things (Rabier, *et al.*, 2006; Temmerman, *et al.*, 2006). These can be relatively straight-forward to assess and is simply a mass-to-volume ratio. This can be done prior to and after pelletisation and the increase in density due to compaction and fluid expulsion can be determined. Alternatively, more complex methods can be employed, of which Rabier, *et al.* (2006) evaluate several, including stereometric methods, and liquid and solid displacement; although they note that several standards for this exist, there is not an entirely uniform method. Of these, solid or liquid displacement techniques were found to have higher reproducibility and repeatability; this buoyancy method using liquid was utilised and described by Temmerman, *et al.* (2006). The pellet in question is weighed in both air and liquid, usually water, and the volume is computed once the density of the liquid is determined. Sometimes, a wetting agent is also added to the liquid to reduce surface tension and ensure that the liquid penetrates the pellets and fills the pore spaces. Rabier, *et al.* (2006) came to these conclusions after testing the pellets used for the durability assessments performed by Temmerman, *et al.* (2006), described above for selection 1 pellets and the briquettes.

The porosity, the void space in the material, indicates the absolute density of the material; as the bulk density increases during pelletisation, the porosity will decrease. Burchill, *et al.* (1994) identifies that if the porosity of the material after pelletisation is high, this ultimately leads to poor pellet quality due to the fragility of the material and thus breaking when shear stress is exerted. Porosity can be generally related to tensile strength and would indicate that the pressure used was not sufficient for that particular material.

5.7.5 Burning Quality and Smoke Measurement

The burning quality and smoke measurement are standard tests carried out for fuels and fuel pellets. The former can be tested by combusting a known quantity of fuel and assessing its performance. These tests usually include some evaluation of the ease of ignition and heat radiation (Jones, 1969). Smoke measurement also takes the form of burning a known weight of fuel and comparing it to the weight of smoke produced; this assesses the fuel quality but is not a control method (Jones, 1969).

5.7.6 Ash Content and Other Chemical Analyses

The ash content often determines the burning quality of fuel pellets, as well as how cleanly they combust (Jones, 1969). Large quantities of ash are detrimental and can decrease the CV notably, thus some ash may be removed if the proportion is large. The chemical components of the materials can affect the physical properties and thus are able to significantly alter the results of the above assessments, such as the affect of ash on CV. Chemical analyses include the determination of the CV, if fuel pellets are to be made, as well as an examination of the constituents, such as ultimate, proximate and elemental analyses.

5.8 MANIPULATION OF PELLETISATION VARIABLES

5.8.1 Variables to Control and Their Effect on Pellet Quality

A number of variables can be controlled and altered during pelletisation to modify pellet qualities. This section aims to report the outcomes of studies that have varied key pelletisation parameters. It is vital that preliminary experiments are undertaken to assess the effect of these on the chosen materials; from this, optimum pelletisation can be achieved, forming high quality pellets.

5.8.1.1 Moisture Content and Drying

The first variable is the moisture content, either of the initial material or the pellets. Its effect is quite complex and the optimum moisture needs to be determined experimentally, as water is often used as a binder (Section 5.5.5). Sastry (1993) suggests the optimum range is narrow. Confirming this, Li and Liu (2000) found oak and pine sawdust pellets had undesirable qualities when produced with high or low moisture. Pellets with less than 4 % moisture had some ideal qualities but were not maintained, whereas those with more than 13 % had low densities and were not durable; the ideal moisture was 6-12 %, with an optimum of 8 %. Mani, *et al.* (2006) examined this effect for chopped corn stover at 5, 10 and 15 % moisture, where low moisture produced better quality pellets.

Radloff, *et al.* (2004) reported that after coal tailing briquettes are manufactured, they are stacked in a drying shed to cure and harden them. The importance of the final moisture was stressed and thus drying is a significant factor that should not be overlooked; they also claim excess moisture can destroy briquettes of this type. Drying after pelletisation is common, which is influenced somewhat by humidity. Li and Liu (2000) found that pellet drying for oak and pine sawdust took 3 days, so the moisture of the pellet and air were in equilibrium, which had a linear relationship with the relative humidity. For Norway spruce sawdust, however, 25 hours of conditioning was sufficient, although moisture uptake was strongly controlled by the initial moisture (Rhén, *et al.*, 2005). The influence of both initial and final moisture and the consequences of drying thus have clear effects on pellet properties. The use of pellet drying is often limited by economics, where a trade-off between quality and cost often ensues (Lehtikangas, 2000).

5.8.1.2 Pelletisation Pressure, Holding Time and Compaction Speed

Another variable to affect pellet quality is pelletisation pressure. Pellet density increases with pressure, due to greater compaction, which is assumed to be strongly correlated with compressive strength, as Rhén, *et al.* (2005) discovered for Norway spruce sawdust pellets. It was also suggested that compaction pressure should not exceed 50 MPa, as these compression forces do not have a significantly greater impact. This, however, does not always greatly influence mechanical durability, at least for the materials investigated by Lehtikangas (2001) and as suggested by Obernberger and Thek (2004); the lignin contents of sawdust, logging residues and bark did however increase pellet durability in their study. A related factor is the holding time at this pressure, which can have a noteworthy effect on density (Li and Liu, 2000). Oak sawdust pellets held for 5 s had low densities, but this increased with holding time; the effect became inconsequential however when this exceeded 20 s and it did not influence the expansion rate after pelletisation. This is thought to be more important at low pressures, where at higher pressures, it can become almost insignificant. Jones (1969) also reported experimental research in this area; holding times up to 64 hrs were used and a clear association for all substances over a range of timescales was found. Another related influence is compaction speed, which is also thought to moderately control density. Slow speeds (<1 MPa/s) may result in higher densities, whereas speeds over 3 MPa/s may not further increase density (Li and Liu, 2000). This affects the commercial manufacture of pellets more so than the results of this study, as using a manual pelletiser will ensure slow speeds; commercial-scale pelletisation, on the other hand, will require rapid compaction to meet high production rates (Li and Liu, 2000).

5.8.1.3 Temperature

The temperature at which the pelletisation takes place can influence pellet properties, where high temperatures can simplify pelletisation and increase compressive strength. Ellison and Stanmore (1981) found this to be true for brown coals, increasing the compressive strength threefold using temperatures of 130 °C. Rhén, *et al.* (2005) found that high temperatures combined with limited moisture increases dry densities for Norway spruce pellets. Increased temperatures may release self-binding agents, such as coal tar, or initiate the softening of lignin and cellulose in biomass.

5.8.1.4 Pellet Size and Shape

Manipulating the shape of the mould changes the size and shape of pellets, which are also thought to affect their properties, such as pellet strength (Patrick and Wilkinson, 1978). Rahman, *et al.* (1989) investigated the effect of dimensions for cylindrical char briquettes with a water additive and a starch-based binder, finding the compressive strength was approximately ten times greater when the plates were in contact with the line of points. Pillow-shaped briquettes had noticeably lower compressive strengths. Altun, *et al.* (2004) examined the variation in combustion kinetics with the size of coal briquettes, assessing the resultant gas composition; experiments determined the effect of increasing briquette size by assessing those of constant volume and different dimensions. Size variation was a significant factor that influenced combustion kinetics and the probability of ignition. The activation energy required to initiate such reactions was also found to increase with size. Furthermore, compact briquette geometries, length-to-diameter ratios near 1, decreased the activation energy and assisted combustion; difficulties were discovered when this ratio approached 2. The geometric area was thought to have a trivial impact.

5.8.1.5 Storage Conditions and Duration

The duration and conditions of storage can alter pellet properties. Lehtikangas (2000), through looking at the storage of biomass pellets, established that although the alterations after storage were not necessarily large, they were noteworthy and depended on the material and the type of storage. Modifications for unpelletised material were compared to sawdust, logging residues and bark pellets. Durability declined, particularly for fresh pellets and breakages were common for extended storage in large bags. Microbial growth was also noted, where temperature development occurred due to insufficient cooling. Moisture was found to decrease and reached equilibrium at ~11 % (Lehtikangas, 2001).

5.8.1.6 Other Variables that Influence Pellet Quality

Other factors can alter pellet quality, including binders (discussed above) and the type and properties of the materials, such as the particle size distribution and composition. Li and Liu (2000) examined the effect of material type, finding bark was easier to pelletise than wood, and hardwoods were more appropriate than softwoods. They also found mulch easier than both sawdust and chips. The curing time may also affect the compressive strength and could alter the functionality of the binder, depending on the length of curing at room temperature, as considered by Blesa, *et al.* (2003).

5.8.2 Optimum Pellet Qualities

According to the above discussion of quality assessment and the influential variables, the following outlines the optimum properties for pellets and the conditions under which these are formed. Whilst some general trends were shown, substances vary and optimum conditions must be determined experimentally for each material. Due to this, it is important to realise there are no general guidelines for optimum pellet production, as properties are extremely dependent on the material; one key example is that the most favourable moisture varies with material, thus an optimum must be established via experimentation.

Pellets with high compressive strengths, usually formed at high pressures, are beneficial so transport and storage does not damage pellets, which can be achieved by altering the pelletisation method, such as adjusting the moisture. Air-curing or making efficient use of a binder also aids this (Plancher, *et al.*, 2002; Sharma, *et al.*, 2002). Density and compressive strength are intimately related; Jones (1969, p49) states: "there is a close relationship between the hardness of a compact and its density, that compaction is achieved by the application of pressure, and that the density . . . at any pressure is influenced by the size distribution . . . and by its elastic and plastic properties." Compressive strength and density thus determine, at least in part, durability. Pellets that are hard, in terms of strength and not brittleness, are more durable and can better withstand testing for such properties.

5.9 PELLETISING BIOMASS AND COAL TAILINGS

5.9.1 Biomass Pelletisation

Pellets can be manufactured from a variety of biomass types, discussed in Chapter 2. Due to the growing demand of biomass resources to increase the proportion of energy obtained from renewables, there has recently been a significant increase in the use of herbaceous crops, wastes and woody biomass, particularly hardwoods, although those most frequently produced are from forestry residues and softwood sawdust (Holm, *et al.*, 2005). In 2002, a pellet conference was held in Sweden, to gather people from industry and research, who work in this field; Vinterbäck (2004) reported the economic, environmental and technological outcomes. The main focus was to aid the implementation of wood pellets, where their production and combustion were considered. The conclusions state that such biomass processing has the potential to replace significant amounts of fossil fuels for heat and power generation; the costs of these are being reduced and the environmental aspects improved.

Holm, *et al.* (2005; 2006) compared the pelletisation of softwood pine shavings to that of hardwood beech dust (Figure 5.11). They explored the factors affecting the process and the pellet properties by combining experimental procedures and theoretical modelling, to delineate the controlling physical and chemical mechanisms of pellet quality. Pine pellets were highly durable and simple to produce, forming only small amounts of dust. In contrast, beech dust pelletisation was somewhat problematic, as the dust caused the motor current to increase, often to critical levels due to blocking. Various additives were used to enhance the procedure; 1 wt% of calcium soap lowered the energy required, but decreased pellet durability. A 40:60 beech-pine mixture, an 85:15 beech-brewers spent grain mixture and inorganic additives mixed with the grain before being combined with the beech were easier to pelletise and resulted in improved pellet quality. From this, a novel theoretical model was used to estimate the necessary pressure; the exponential relationship with channel length was dependent on the matrix dimension, sliding friction coefficient, the specific elasticity modules and Pisson's ratio of the biomass. It was predicted that the pressure for beech would increase more rapidly than for pine. The differences highlighted in these papers are thought to be primarily due to the variation in cell structures between hard and softwood types; these results can be extended to other types of biomass, such as grass, animal wastes and aquatic vegetation.

(a) (b)

Figure 5.11: Photographs of the pelletised (a) pine shavings and (b) beech dust.
Source: Holm, *et al.* (2005)

Demirbaş and Şahin (1998) investigated pelletised wheat straw and waste paper. The ideal moisture was 18 % for a mixture containing 20 wt% paper; at this moisture, the compressive strength was 32 MPa. It was possible to form pellets without a binder, as the paper partially performed this function, however, it was problematic at ambient temperature; on heating the straw to ~400 K, the pellets were of considerably better quality. Gilbert, *et al.* (2009) found that simply cutting switchgrass formed the best fuel pellets; shredding produced pellets that were not as robust, but were better than when the material was torrified. When combined with heavy pyrolysis oil, used as a binder and supplementary fuel, the product was much stronger. As with the above study, temperature was also highly influential, due to the lignin content. Yaman, *et al.* (2000) researched olive refuse and paper mill waste pelletisation. The particle sizes were reduced to 250 μm and then pelletised at 150-250 MPa. The combination of these substances produced significantly better quality pellets than just olive waste, which had low compressive strengths. Li and Liu (2000) utilised a range of wood-based materials to form pellets (Figure 5.12). From various tests performed on these, optimum conditions for pellet manufacture were determined. High densities could be achieved in many cases, which facilitated storage and transport; the densest pellets also had a higher energy density, which were ideal for coal co-firing. Sugar cane bagasse and corn stover have also been considered in this context (Erlich, *et al.*, 2005; Mani, *et al.*, 2006).

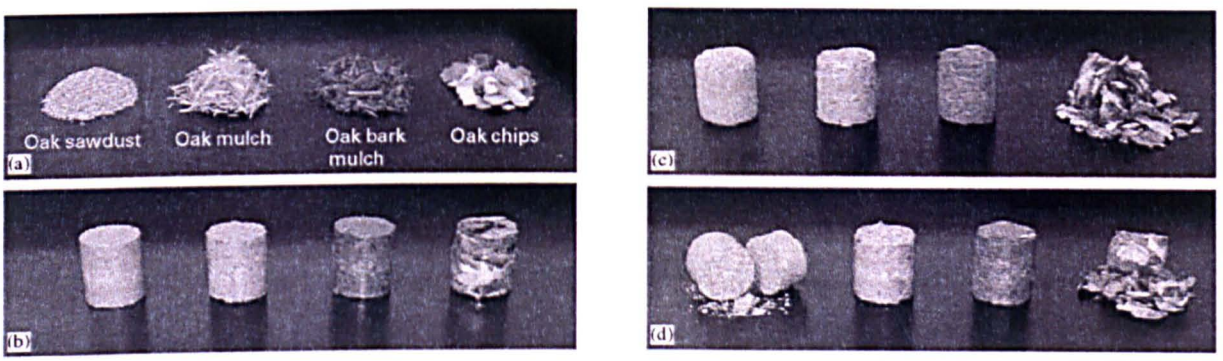


Figure 5.12: Photographs of the biomasses used for pelletisation. (a) The initial materials; (b) pellets compacted at 138 MPa; (c) results of the tumbler tests and (d) results of the drop tests.
Source: Li and Liu (2000)

5.9.2 Coal and Coal Tailing Briquetting

Briquetting specifically concerns coal tailings and lower-ranking and low CV coals, which may otherwise be disposed of, as they have only a modest commercial value (Berkowitz, 1979). The briquetting of coal

tailings can alleviate the dust hazards associated with this waste (Sastry, 1993). The use of coal as a fuel is obviously not new and therefore its treatment processes are well-developed. Briquetting was initially designed to produce a smokeless fuel from lower-rank coals; the particle sizes of these fractions were fine and thus agglomeration was needed (Jones, 1969). It is often difficult to form durable briquettes from this type of material, even when it is crushed and the moisture adjusted to act as a lubricant (Messman, 1977). If pulverised and prepared correctly, however, durable briquettes can be formed, with or without a binder (Berkowitz, 1979). For binderless briquetting, coal is usually heated to low temperatures to increase plasticity; maximum plasticity of low-ranking coals is achieved at 400 °C (Jones, 1969). Akgun, *et al.* (1989) found that briquetting lignite, even at temperature did not form a coherent, quality product. The extrusion of run-of-mine brown coals after attrition, however, formed hard briquettes (Johns, *et al.*, 1989).

Briquetting with a binder, depicted in Figure 5.13, is distinctly different to that of binderless briquetting. Drying and grinding the material are important preparatory phases, and mixing and tempering the material-binder mixture are also vital (Berkowitz, 1979). The binder quality and quantity are of utmost importance (Berkowitz, 1979; Paul, *et al.*, 2002). Burchill, *et al.* (1994) used molasses and modified starch, whereas Paul, *et al.* (2002) investigated petroleum residues for formcoke briquettes. Binder oxidation strengthened briquettes, influenced by the air curing time and coking. Studies have also concerned coal tailing briquetting. Richards (1990), though looking primarily at producing good quality binderless briquettes of peat and coal-peat combinations, found that peat acts as a binder in the briquetting of sub-bituminous coal fines. Radloff, *et al.* (2004) favoured binder briquetting, and although their product was of good quality (Figure 5.14), the binder used was not described.

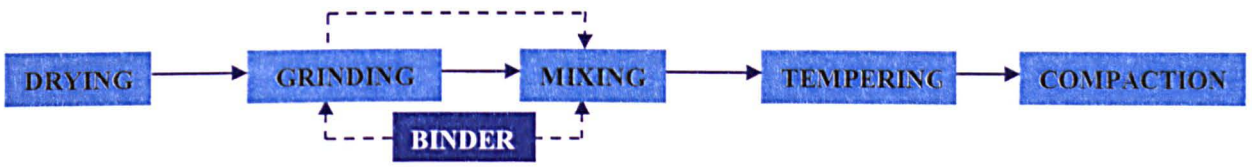


Figure 5.13: The manufacturing process for coal briquetting with a binder.
Source: Berkowitz (1979)

Figure 5.14: Briquettes of coal tailings formed with an unspecified binder.
Source: Radloff, *et al.* (2004)

5.9.3 Producing Pellets from Spent Mushroom Compost and Coal Tailings

Coal tailings and SMC could be combined to produce fuel pellets; it is essential that these are prepared and combined prior to pelletisation. As has been discovered, the composition is not ideal and thus drying will need to take place, to ensure better product and fuel qualities. Some form of post-production

treatment may be necessary to enhance their properties, such as further drying. As many pelletisation variables can be adjusted, it is important that a range is explored to ensure the optimum conditions are used and therefore the best quality pellets are formed. It is thought that the coal tailings would act as a binder and a secondary fuel; this dual-functionality was considered in more depth previously.

The economic feasibility of pellet production from the materials depends on many factors, including those associated with their alternative uses. Unfortunately, the costs and availability of other fuels influence the overall viability of this too. The cost of producing these pellets therefore needs to be compared directly with that of disposing of SMC in landfill. The environmental costs should also be taken into account when the two are compared. To properly assess the economics of pellet production, a full cost analysis will be required, as outlined in Section 5.6, to account for all pelletisation and thermal treatment costs. The transport and storage costs of the raw materials and pellets will also need to be considered. The final cost will be the overall total of producing pellets; this can be compared to the other uses of these materials and their disposal. If SMC is no longer allowed to go to landfill, this will improve the economics; this, in addition to the value of removing coal tailings from lagoons, will also bring environmental benefits.

There are many potential uses of SMC-coal tailing pellets; they could be used to produce energy through combustion, or possibly gasification or pyrolysis. Alternately, they could be used as a supplementary or auxiliary fuel, through co-firing with coal or natural gas, as explored by Williams, *et al.* (2001a), or also other biomass or waste materials, as considered by BioMatNet (2004). There are several environmental considerations that need to be taken into account when producing and using these fuel pellets. Apart from the emissions produced, the overall environmental impact will be positive. Many aspects of this have been considered previously, in relation to each material; using SMC will avoid landfill and will also increase the amount of energy coming from renewable sources and as it is carbon-neutral, it will not be adding to the greenhouse effect. The use of the coal tailings will aid the clean-up of contaminated land.

Pelletising a combination of biomass with coal or coal-derived products is not new. The investigation by Yaman, *et al.* (2001), for instance, concerned the pelletisation of lignite and various types of biomass. Pellets were formed with different ratios of materials (0-30 wt%) and at varying pressures (50-250 MPa). The strength of lignite briquettes could be increased with additions of sawdust and paper mill waste; the effect of olive refuse, however, was detrimental. This study further confirmed the results of Yaman *et al.* (2000), discussed above. Zhang, *et al.* (2001) examined differing biomass treatments to form a binder for lignite briquettes; rice straw was treated with a number of chemicals (sulphuric acid, lime and sodium hydroxide) and was then used via the process summarised in Figure 5.15. They found that the type and concentration of chemical was influential; furthermore, temperature was a prominent influence. Of the chemicals tested, lime and sodium hydroxide were superior and supplementary additions of bentonite, coal tar and/or polypropylene amide made the pellets more water resistant. Sodium hydroxide was able to bond in both its solid and liquor forms.

Figure 5.15: A flow diagram of the materials and processes for forming lignite and biomass briquettes. Source: Zhang, *et al.* (2001)

5.10 SUMMARY

This chapter outlined and described the fundamental theory inherent to pellet formation. The pelletisation of substances to produce homogeneous, consolidated pellets of uniform size was explored. The main advantages of pelletising fuels are the increased bulk and energy densities and the control over moisture, both of which are particularly relevant to biomass fuels, as these tend to have low densities with high moisture. Pelletisation can be classified in many ways, based on the pressing process or pressure used; pelletisation below 7000 psi (48 MPa) is categorised as low pressure. The two major types of pelletiser technology, extrusion and compression were examined – this is another type of classification. Extrusion forces the material through an orifice to form pellets, whereas compression is where the substance is consolidated in a mould by applying pressure. The compacting sequence for the latter was outlined as charging, pressing and ejecting. Naturally-occurring particle binding and agglomeration were explored; if cohesion is insufficient, a binder can be used to enhance or promote agglomeration phenomena. The economics were documented and the main costs identified, namely the initial price of the pelletiser, along with its running and maintenance costs. Transport and storage can also be costly, especially for materials with a low bulk density or a high moisture content, such as many biomass fuels, like SMC.

Various methods for pellet quality assessment were outlined, which can be used in the experimental stage of this investigation. Techniques of particular relevance were the compressive and tensile strengths and durability. The methods identified for many of these criteria were not standard, as these often do not exist. Pelletisation variables that control these qualities were explained; the most significant included moisture, drying, pelletisation pressure, temperature and the length and conditions of storage; these are key variables to explore herein. Using appropriate conditions, good quality pellets can be produced, which would be durable and have high tensile strengths; unsuitable conditions lead to the formation of a poor quality product, which can break easily and would be unsuitable for their intended purpose.

Previous studies have examined biomass pelletisation (forestry residues, herbaceous crops and wastes) or coal briquetting, though only a few explored the pelletisation of these combined, which is the focus of this research. From a review of these, the pelletisation procedure for SMC-coal tailing pellets was outlined. This would involve preparation, such as drying, and their combination prior to pelletisation; post-treatments, for example additional drying may also be required. Furthermore, the potential uses of these pellets were considered, such as energy generation through combustion on their own or for co-firing as a supplementary fuel. The environmental benefits were also discussed, including the carbon-neutral nature of the SMC and the minimisation of both these wastes being disposed of in unsustainable manners.

6

ANALYTICAL METHODS FOR MATERIAL CHARACTERISATION

6.1 INTRODUCTION

The experimental phase of the investigation was divided into three distinct stages. The initial one was the characterisation of the materials, to determine their composition and properties. This included a number of standard analytical tests: proximate, ultimate and elemental analyses and the determination of the CV. The material particle size distributions were also established. These tests were performed on the coal tailings and the two SMC components separately.

6.2 EXPERIMENTAL METHODOLOGIES

This section outlines the techniques used to analyse the materials, introduced briefly in Sections 2.2.6 and 5.7.6. This includes details of the proximate, ultimate and elemental analyses, as well as CV tests, in accordance with British Standards. The experimental accuracy and errors are also considered here.

6.2.1 Proximate Analysis

Proximate analysis was used to determine the composition on a constituent basis (Speight, 1994). This form of analysis involved determining the moisture through drying, the volatile matter by 'inert devolatilization' and the ash content, the residue remaining after complete combustion in air; the fixed carbon was found by difference. The method used was the British Standard 1016, Part 3: 1973 (British Standards Institution, 1973).

6.2.2 Ultimate Analysis

The ultimate analysis determined the absolute elemental composition (Speight, 1994). This test was carried out by the Centre for Analytical Sciences at the University of Sheffield. From this, the percentages of C, H, N, S and Cl were established, and O by difference. The sample was ground, passed through a British Standard sieve (No. 72 or 212 μm) and left to equilibrate with the laboratory atmosphere; it was then burned in pure oxygen at 1350 °C, according to the British Standard 1016, Part 6: 1977 (British Standards Institution, 1977a).

6.2.3 Elemental Analysis

The elemental analysis determined the proportions of additional key and trace elements compared to the ultimate analysis. The process by which an elemental analysis is undertaken is complex and thus cannot be given a full explanation in the scope of this research; there are many papers that use variations of this method, such as Ashley, *et al* (2001). An overview of the procedure is that a small but representative sample underwent acid digestion by titrations using nitric and hydrochloric acids. This enabled the constituents to dissolve and the proportions of different elements were then determined by ICP-MS (inductively-coupled plasma mass spectrometry) detection using a Spectro Cirus ICP atomic emissions spectrometer. This gave the composition of the material, focusing specifically on the metal contaminants, in particular the alkali, transition and heavy metal content. Over 95 % of the constituents can be established in this way, although fibrous material, such as that in the SMC, did not fully dissolve and therefore not all elements were determined. These experiments were also performed by the Centre for Analytical Sciences.

6.2.4 Determination of Calorific Values

To establish the CV, the enthalpy of combustion described in Section 2.2.3.1, 1 g of sample was combusted in controlled conditions, of which there are several standard methods (Speight, 1994). Here, a bomb calorimeter was used under standard conditions (temperature = 298 K and pressure = 1 bar), as it is thought to be the most accurate method; this follows the British Standard 1016, Part 5: 1977 (British Standards Institution, 1977b).

6.2.5 Particle Size and Particle Size Distribution

In order to determine the particle size and distribution, different methods were employed due to the variation in the materials. The particle sizes of the coal tailings and the SMC casing layer were both reasonably small and were established using a series of British Standard sieves of different sizes (BS410), as described in Section 5.7.1. The distribution of particle sizes was calculated by weighing the fraction of the material in each sieve. As some agglomeration of these materials had already occurred, the absolute particle sizes were not measured but the agglomerate size distribution instead. For the substrate layer of the SMC, an alternative method was used as there was great variety in particle size. As this is composed

primarily of straw, there were long, thin fibres, of which a representative sample was chosen and the fibre lengths were measured with callipers.

6.2.6 Experimental Measurement Accuracy

The main error in this experimental approach was accuracy; specifically sample weights and the length of time samples were left in the furnace. Although a balance accurate to 0.0005 g and a stopwatch accurate to the nearest 0.5 s were used, errors to a certain extent were still likely to be introduced here, though they were thought to be small. There were also likely to be sampling errors. The samples chosen may have not necessarily been representative of the material as a whole, as the SMC in particular was not homogeneous; to overcome this, several samples were taken and the experiments were repeated and the results averaged. Additional errors were present in the analysis, due to inaccuracies in the equations utilised. Errors that were introduced in the experimental stage also advanced to here and even if these were small, as fixed carbon and oxygen were determined by difference, it is likely that errors would have accumulated here. The most inaccurate values were for the proximate analysis, particularly on a dry, ash free basis ('daf'), which were likely to contain large errors. Those concerning the measurement of the particle size and distribution were primarily the accuracy of measurement (± 0.5 mm for the fibres) and the sampling error.

Montgomery (1978) examined a number of errors that may occur in the determination of the CV; these included human errors (recording temperatures and weights, and in calculations), inaccurate or poorly calibrated equipment, incomplete combustion, a tarnished or corroded bucket, changes in heat capacity of the system due to replacement of parts and bomb leakage. It is thought that only the first was likely to impact the results to any degree, although other errors may be present. The main sources of error here were thought to be those apparent in the data and equations. Accuracy, mainly the weight of the samples (balance accurate to 1 mg) may be problematic. Errors may also be evident in the analysis; errors introduced in the experimental stage would again have advanced to here.

6.3 RESULTS & ANALYSIS OF MATERIAL CHARACTERISATION

This section reports the experimental values gained from each of the material characterisation tests and compares them to data accumulated in the literature, Section 2.4.2.2 for the SMC and Section 2.5.3.1 for the coal tailings. Comparisons to other biomass and waste fuels detailed in Section 2.2.3 are also made here.

6.3.1 Results of the Proximate and Ultimate Analyses and the Calorific Value

The three samples, the coal tailings and the two SMC layers, were analysed according to the standard methods outlined above; averaged results for proximate, ultimate and CV analyses are given in Table 6.1.

The moisture content of the materials were determined on an 'as received' (ar) basis; these all initially have very high moisture contents and thus significant drying will need to occur before pelletisation. This will also be necessary prior to their use as fuels to enhance their CV, as the effects on this were clearly apparent. The moisture content of the coal tailings was similar to those outlined in Table 2.16 and that of the SMC layers were comparable to those reported by Williams, *et al.* (2001a).

ANALYSIS	CONSTITUENT	BASIS	COAL TAILINGS	SMC SUBSTRATE	SMC CASING
Moisture (%)		ar	~40	65.70	68.56
Proximate Analysis (%)	Ash	dry	41.25	26.89	28.87
	Fixed Carbon		38.24	11.31	10.95
	Volatiles		20.51	61.80	60.18
	Fixed Carbon	daf	65.08	15.48	15.40
	Volatiles		34.92	84.52	84.60
Ultimate Analysis (%)	C	dry	47.87	35.13	35.72
	H_{true}		2.90	3.59	3.01
	N		1.01	2.85	1.11
	Cl		-	0.51	0.70
	S		1.38	2.95	2.16
	O (difference)		3.69	19.50	20.09
CV (MJ/kg)	GCV	ar	11.91	4.94	4.33
	GCV	dry	19.85	14.11	12.37
	NCV	ar	10.55	3.08	2.51
	NCV	dry	19.22	13.33	11.71

Table 6.1: Averaged results for the proximate, ultimate and CV analyses for the three samples.

For the proximate analysis, the ash and volatiles were determined and these values were utilised to convert the raw data to a dry basis and then calculate the fixed carbon by difference. These results also enabled the determination of the fixed carbon and volatile content on a 'daf' basis. The proportion of ash in the coal tailings was high, yet comparable to the results of Sis, *et al.* (2004) and Radloff, *et al.* (2004); Sabah *et al.* (2004) reported a much larger ash content for their coal tailing sample. The results for the two SMC layers were in fact highly analogous and were also very similar (towards the lower end of the range) to those of Williams, *et al.* (2001a); they did not, however, analyse their samples separately, and therefore their results were averages for the substrate and casing layers. The volatiles and fixed carbon content of the SMC layers were again equivalent to those of Williams, *et al.* (2001a). No values were available for the comparison of the coal tailing samples. The coal tailings had a larger quantity of fixed carbon compared to the SMC layers, but appreciably less volatile matter. Various types of biomass used for energy recovery were discussed in Section 2.2.3; although the components of these vary considerably, the high volatile content and low fixed carbon of the SMC samples were comparable to these. The ash content of SMC, however, was significantly higher than those considered in Table 2.5.

The C, H, N, S and Cl were determined for each substance, after which H_{true} was calculated, and the O content was established by difference. As these constituents contribute only 60-75 % of the total, the O content was likely to be highly inaccurate. Other important elements were subsequently characterised by the elemental analysis. Approximately half of the coal tailings were composed of carbon in some form;

other elements, H, N, S and O made up only a small proportion and there was no Cl present, which is advantageous in terms of the emissions that may form. Results of an ultimate analysis for coal tailings could not be found in the literature, so there was no basis for comparison. The results for the SMC layers once more suggest that they were quite similar; the N content differed the most between the two (1.74 %). Although S and N were abundant, it has been found from previous literature that these should mainly be bound in inorganic forms, and thus using a fluidised-bed combustor will minimise the risks of forming NOx and SOx (Williams, 2001; Williams, *et al.*, 2001a). The percentages of these however were significantly higher than other types of biomass considered in Table 2.4; conversely, the C and O contents were comparable with these other biomasses. Williams, *et al.* (2001a) had corresponding results to these (Table 2.11), particularly for C, N, S and Cl; the O content herein was slightly lower.

The GCV of the samples were determined on an 'ar' basis; the dry GCV and NCV were computed from these. Dried coal tailings have a moderate CV; this was comparable to sub-bituminous C coal and the coal tailing samples discussed in Section 2.5.3, which had a range of 16-22 MJ/kg. The CVs of the two components of the SMC were congruous, where the substrate has slightly more energy content, equivalent to those of group B lignites; their CV was significantly lower than the coal tailings. As such, additions of SMC to the fuel pellets will lower their overall CV. These values are however similar to those of Williams, *et al.* (2001a); in this study, the effect of high moisture contents on the CV was seen (Table 2.12), highlighting the need for drying these materials, which was also apparent from the results above. In addition to relating these to various ranks of coal, the CVs can be compared to the biomass fuels described in Table 2.2. The CV of the coal tailings was analogous with other types of fuels, such as miscanthus, pine and RDF. The CV of SMC was lower than many of the biomasses outlined, as only MSW and gasified wood chips had lower CVs, although previous studies of SMC have not reported this to be problematic. MSW, however, has a considerably lower CV than SMC and this is already used for energy generation, further ensuring that the moderate CV will not affect its use as a fuel.

6.3.2 Results of the Elemental Analysis

The results of the elemental analysis are shown in Table 6.2; averages are given, as the tests were repeated due to the lack of homogeneity of the materials, especially for the SMC. This analysis highlighted the differences between the two SMC layers, as more elements were identified. Elements that may cause problems during combustion were also acknowledged. Sulphur was found in significant concentrations, as shown by the above analysis, which may form SOx. Whilst this form of acid gas is thought not to form due to the inorganic origin of most of the S, the large proportion of Ca in the material could further minimise the formation of this pollutant, effectively acting in a similar manner to a sorbent injection; P was also found in notable amounts, however, which is known to impede this mechanism (Williams, *et al.*, 2001a; Elled, *et al.*, 2006; Altun, *et al.*, 2006). This relatively high concentration of S, in the SMC, and coal tailings to a lesser extent, however, could inhibit *de Novo Synthesis*, thus preventing the formation of dioxins and furans, as Cl was present in the SMC (Fielder, 1998).

ELEMENT	AMOUNT (mg/kg)		
	COAL TAILINGS	SMC SUBSTRATE	SMC CASING
Al	4360.0	441.5	1435.0
As	14.8	<1	<1
B	5.5	24.2	12.6
Ba	231.0	65.3	77.2
Ca	2940.0	40900.0	118500.0
Co	9.7	1.0	0.8
Cr	13.0	3.8	6.2
Cu	19.0	46.1	11.7
Fe	9700.0	1240.0	2580.0
K	1070.0	18650.0	3685.0
Li	10.0	1.5	2.0
Mg	2420.0	4620.0	4265.0
Mn	127.0	295.5	138.5
Mo	2.3	4.1	0.3
Na	450.0	2095.0	600.0
Ni	22.8	3.2	2.2
P	74.3	6655.0	4220.0
Pb	12.9	2.6	5.1
S	4180.0	23050.0	3915.0
Si	1380.0	1620.0	1485.0
Sr	24.1	207.5	97.2
Ti	27.8	10.9	37.2
V	10.4	2.3	5.2
Y	1.7	1.2	2.0
Zn	34.6	194.5	44.1

Table 6.2: Table showing the amounts of various elements present in the samples.

The presence of a range of other elements could lead to issues concerning the ash produced on combustion; this includes K, Na, Si, Al, Fe and P. The amount of ash in the initial materials is also high. Alkali metal oxides are the cause of slagging and fouling within combustors, where deposits of ash build up due to its lowered melting point (Jenkins, *et al.*, 1998). K was found to be particularly concentrated in the SMC substrate and this could be problematic. Si in particular, but Al and Fe to lesser extents, also contributes to this problem if found in oxide form and were some of the more prominent elements in the above analysis for all three materials (Öhman, *et al.*, 2004). It is also thought that K, Si, Cl and P can contribute to the agglomeration of the ash formed and as considered, these elements were found to predominate in these materials. (Fryda, *et al.*, 2006). P was more ubiquitous in the SMC layers. Heavy metals were not especially prevalent.

6.3.3 Results for Particle Size and Particle Size Distribution

The particle sizes of 1 kg of the coal tailings and 500 g of the SMC casing were measured using standard sieves (Table 6.3). Some coal tailings had already formed agglomerates, distinctly altering the particle size distribution, thus large particles formed a substantial percentage (61 % > 1180 μm) of the sample. Due to this agglomeration, only a third of particles were below 1 mm, with the mean particle size above 1180 μm; as such, this is not comparable to the results of Sabah, *et al.* (2004) and Franks, *et al.* (2005), considered in Table 2.16. The mean particle size for their samples was very small, ranging from sub-micron to 10 μm.

PARTICLE SIZE CLASS	COAL TAILINGS (wt%)	SMC CASING (wt%)
< 45 μm	0.10	0.03
45 μm	2.25	0.18
75 μm	4.76	0.54
106 μm	3.79	1.45
150 μm	8.91	8.37
355 μm	4.51	6.02
600 μm	4.05	4.79
850 μm	1.65	1.86
1000 μm	2.98	3.55
1180 μm	5.57	10.01
> 1180 μm	61.43	63.20

Table 6.3: The particle size distribution in weight percentages of the coal tailings and SMC casing.

There was also some agglomeration of the SMC casing, where peat particles had bound together, often around fibrous material (partially decomposed wood). Due to this, there was again a large proportion of material above 1180 μm. The size distribution for the rest of the casing layer was also similar to the coal tailings, as a significant proportion of both were classed as 106-150 μm. The initiation of binding between particles in these materials and the subsequent onset of agglomeration were promising for their pelletisation; if these processes occur naturally, then with the aid of pelletisation, the pellets formed should be of a reasonable quality.

The lengths of 100 SMC substrate fibres were measured (Figure 6.1). The results indicate a positive skew, as the majority of fibres were quite short (average 18.9 mm) although there were also a few longer fibres (> 60 mm). It is thought that these long fibres could become intertwined between the smaller particles in the pellets and enhance their strength, which may be particularly true if the pellet dimensions are smaller than the fibre lengths. The majority of fibres were less than 15 mm and therefore the pellet diameters would have to be small. The small particles in the SMC casing layer and in the coal tailings, coupled with the longer, flexible fibres of the SMC substrate encased in these agglomerated particles may enhance the strength of the pellets.

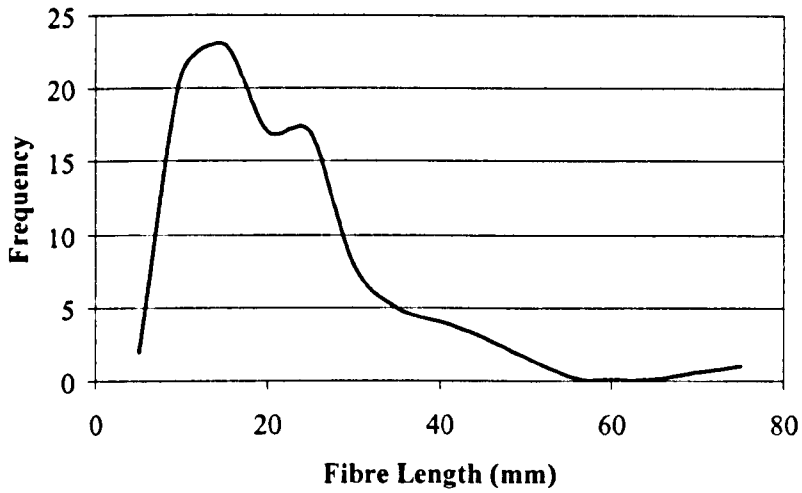


Figure 6.1: The particle size distribution of 100 fibres in the substrate layer of the SMC.

6.4 DISCUSSION OF THE EXPERIMENTAL RESULTS

The analyses of the composition, such as the ultimate and elemental analysis, identified elements that could form gaseous pollutants, such as nitrogen, sulphur and chlorine, which could then produce acidic species in the atmosphere. Potential particulate problems were also identified, due to the high ash content of the materials. This issue could be exacerbated due to the presence of alkali metals and other elements (Si, Al, Fe and P) in the materials if found in oxide form, which could result in slagging, fouling and ash agglomeration if these form metal oxides during thermal treatment. There were not however concerning quantities of heavy metals. Despite their vastly differing physical appearance, the two SMC layers were characteristically alike.

These results also gave an indication of the combustibility of the materials by determining the volatile and fixed carbon contents and were analogous to results found for a range of other fuels in the literature. The CVs of these fuels on a dry basis were comparable to the literature, namely those of Williams, *et al.* (2001a) and Radloff, *et al.* (2004), who analysed SMC and coal tailing samples respectively. These values were also analogous to those of other biomasses and wastes currently used as fuels, thus there should not be a problem using SMC and coal tailings as fuels, once they have undergone a certain degree of drying, as the high moisture contents, particularly for the two SMC layers clearly had dramatic negative effects on the CV. High values for the moisture contents were also reported in the literature.

Furthermore, the particle sizes of each sample were ascertained; it was found that significant agglomeration had already occurred in the coal tailings and SMC casing layer, which had similar particle size distributions. The long SMC substrate layer fibres (10-30 mm) should provide flexibility and strength to the pellets, where the coal tailings and casing layer can agglomerate around the intertwined fibres.

6.5 CONCLUSIONS

The SMC and coal tailings were characterised by their elements, constituents and CV. The ultimate, proximate and elemental analyses divulged important information concerning the constituents that would decrease the CV, specifically the moisture and ash. The CVs were acceptable to use as fuels on a dry basis and were comparable to the literature concerning these and other fuels, however, the moisture clearly needs to be significantly reduced to avoid the obvious detrimental effects to the CV. These tests also identified elements that may form pollutants or cause combustion problems, such as nitrogen, sulphur and alkali metals. These fuels would benefit from pelletisation, where the densities could be increased and the long SMC substrate fibres could intertwine within a matrix of agglomerated coal tailings and SMC casing particles.

7

PELLETISATION EXPERIMENTS

7.1 INTRODUCTION

This second experimental chapter investigates the pelletisation of the two wastes into biofuel pellets. The formation process of the pellets is described, along with the various methods for assessing pellet quality. A range of pelletisation variables that modify pellet characteristics were identified in the review of pelletisation theory in Section 5.8. Based on this, hypotheses were formulated relating to each case study, which assessed and quantified the effect of manipulating these parameters. Here, an optimum value was determined for each to establish the most ideal pelletisation conditions. Although the quality of pellets produced using these optimum values were enhanced, they were still friable – producing dust on handling and feeding. Ways to further improve pellet quality were subsequently examined, including the use of binders, elevated temperatures and steam conditioning. The experimental methodologies employed and the results and statistical analyses gained from these tests are outlined within this chapter.

7.2 PELLET FORMATION

Pellets were produced using a manual pelletiser (Figure 7.1), which worked on the compression principle, as described in Chapter 5.4.1. This pelletiser operated on the compacting sequence outlined in Figure 5.1. For the initial stage of the compacting sequence – charging (Figure 5.1a) – a mass of coal tailings, SMC or the two combined was weighed, between 25 g and 30 g and using a funnel, was placed into the opening in the hollow column at the centre of the pelletiser. The stopper was then placed in the column on top of the material and the screw-on lid fastened. For the second stage, pressing – shown in Figure 5.1b, the handle or lever was used to increase the pressure inside the 26.8 mm diameter chamber by causing the horizontal plate to move up, until the required pressure was achieved, indicated on the gauge; the pressure

indicated on this gauge is 4.06 times lower than the true pressure due to the differences in the areas of the piston and the ram, thus the pressures recorded were multiplied by this factor (for example: 600 psi reading = 2436 psi actual pressure or 16.8 MPa). A stopwatch was used to record the holding time.

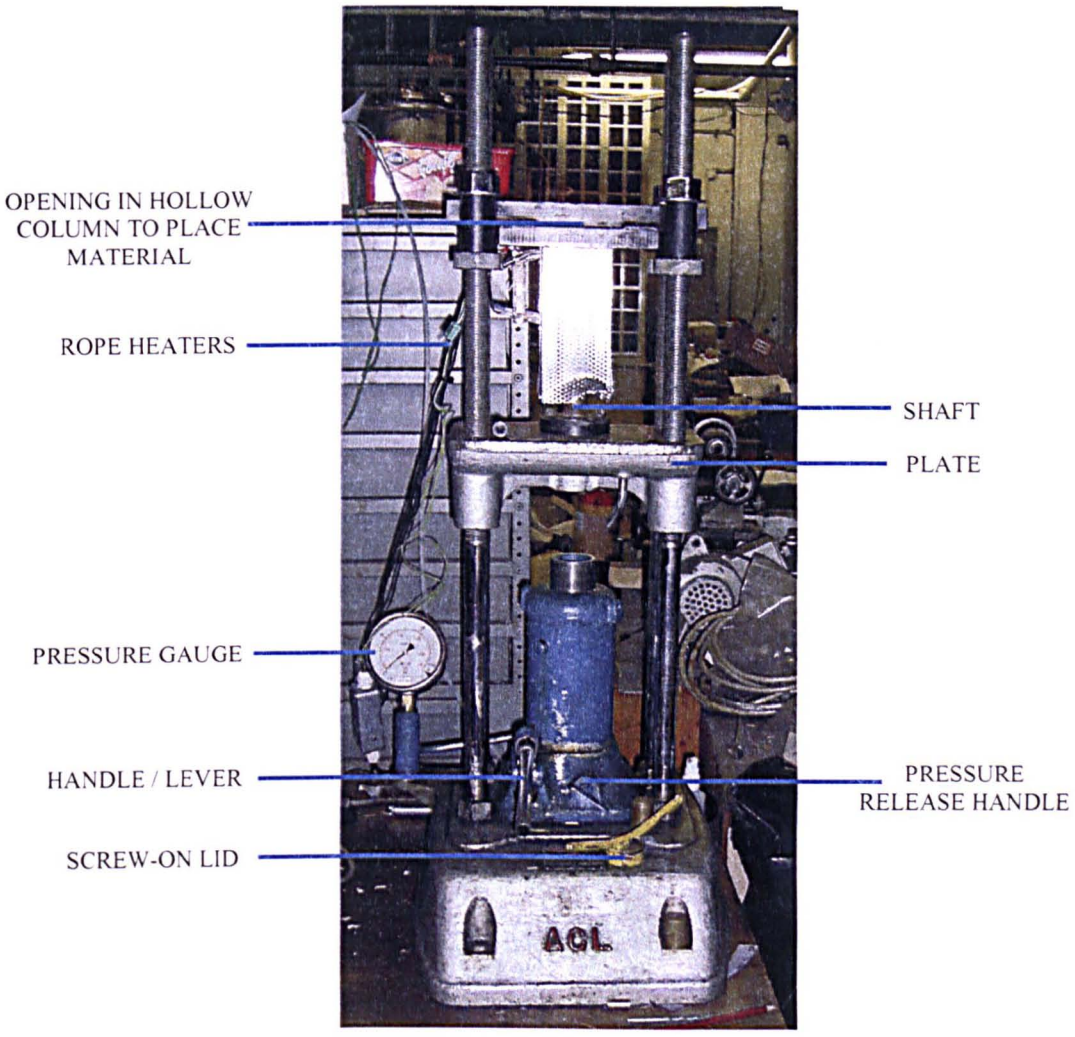


Figure 7.1: The pelletiser used to form the briquettes and pellets.

In the final stage of the compacting sequence, ejection (Figure 5.1c), the pressure was released by twisting the pressure release handle and the plate moved down. The screw-on lid was then removed and the lever was used to increase the height of the plate until the stopper emerged from the column; it was removed and the pellet emerged as the plate was pumped further. Once the pellet had been removed, it was weighed, measured and any further testing or processing took place. In most cases, this involved air-drying the pellets, to improve properties such as the CV and the energy recovery, as considered in Section 5.3.3. There were also rope heaters and thermocouple wires connected to the vertical shaft and a gauge to control the temperature at which the pellet was formed.

7.3 DATA ANALYSIS: ASSESSMENT OF PELLET QUALITY

Once the pellets had been manufactured, key properties were tested to analyse the variation in pellet quality. The four criteria assessed were the pellet density (the weight-to-volume ratio), tensile strength,

pellet pile-up results and pellet durability, which were averaged for 5 pellets in each case. The details for each assessment technique are given below; these were identified in Chapter 5.

7.3.1 Density and Tensile Strength

Pellet density, described in Section 5.7.4, was computed by producing a ratio of pellet weight to its volume, in kg/m^3. Tensile strength, introduced in Section 5.7.2, was assessed using the Brazilian test, where a Monsanto tensometer, shown in Figure 7.2, measured the force that the pellet can withstand; this is an indicator of cohesion (compressive strength) related to pellet size and shape. To measure this, a pellet was placed between the tensometer plates and held with minimum force. The measurement gauge was then set to zero and the handle rotated to apply pressure, where the maximum radial force was recorded before the pellet failed by deformation or fracture (breaking/cracking). The radial forces measured would be lower than the axial forces that pellets of this shape (cylindrical) could withstand.

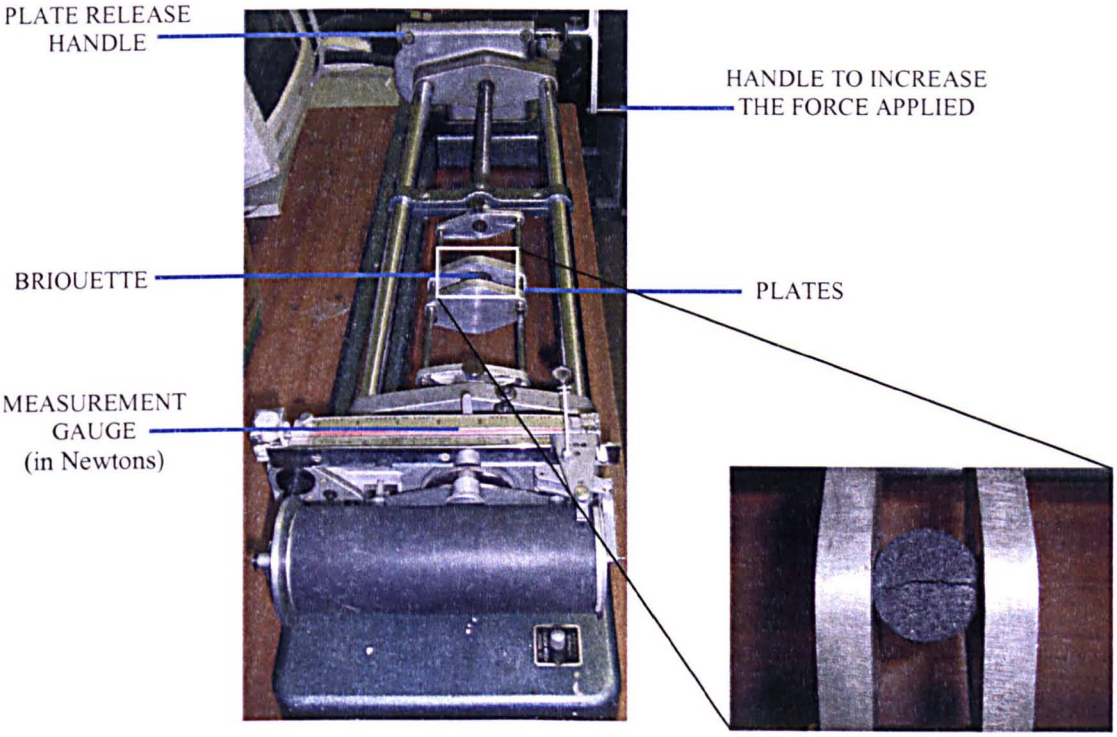


Figure 7.2: Monsanto tensometer for testing tensile strength, with a coal tailing briquette example.

Since the compressive strength was measured but the tensile strength was required, the following equation was employed, which utilises additional information concerning the length and diameter of the pellets to convert the values obtained and relate it to the shape and size of the pellet:

$$TS = \frac{2000 \times CS}{\pi \times L \times d} \tag{7.1}$$

where TS is the tensile strength in kPa, CS is the compressive strength gained from the tensometer tests in N, L is the pellet length and d is the pellet diameter, both in mm. Single factor (one-way) analysis of variance (ANOVA) tests were completed to indicate the statistical significance of the differences found; *P-values* of less than 0.01 suggest that the difference between the data sets compared were significant.

7.3.2 Pellet Pile-Up Tests

The data for diameter, length, density and compressive strength from the above experiments were then manipulated to calculate the weight, number of pellets and subsequent maximum height of a pellet pile, relating it to the pressure and weight that the pellets at the bottom could withstand. Initially, the overall bulk density of the pellets (ρ_{pellet} in kg/m^3) was required along with the average pellet dimensions (in mm); from this, the mean weight per pellet (W_P) in kg was calculated:

$$W_P = \frac{\rho_{pellet} \times L \times \pi \times d^2}{4 / 1000000} \tag{7.2}$$

By utilising Newton's Second Law of Motion, the maximum weight, W_{max} in kg, was computed:

$$W_{max} = \frac{CS}{9.8} \tag{7.3}$$

The number of pellets ($P_{no.}$) in a pile of maximum height that those at the bottom could withstand was determined by:

$$P_{no.} = \frac{W_{max}}{\text{weight per pellet}} \tag{7.4}$$

Using this and the pellet diameter, the maximum height of an ordered pellet pile (H_P in m) was calculated:

$$H_P = \frac{P_{no.} \times d}{100} \tag{7.5}$$

Random packing in a real pile would however result in a significantly greater depth.

7.3.3 Determination of Durability

The durability of pellets was assessed to determine the most robust, and indicated the ability of the pellets to absorb mechanical shocks and withstand abrasion, friction and vibrations, simulating the conditions experienced during transportation and handling. For each case, five pellets (restricted by drum capacity) were placed in the 100 mm x 200 mm cylinder containing a small baffle and mounted into a lathe, which rotated at 40 rpm (Figure 7.3). The drum was rotated for 20 mins, a total of 800 revolutions, and the weight of the pellets that were intact and the larger pieces were measured at 5 minute intervals.

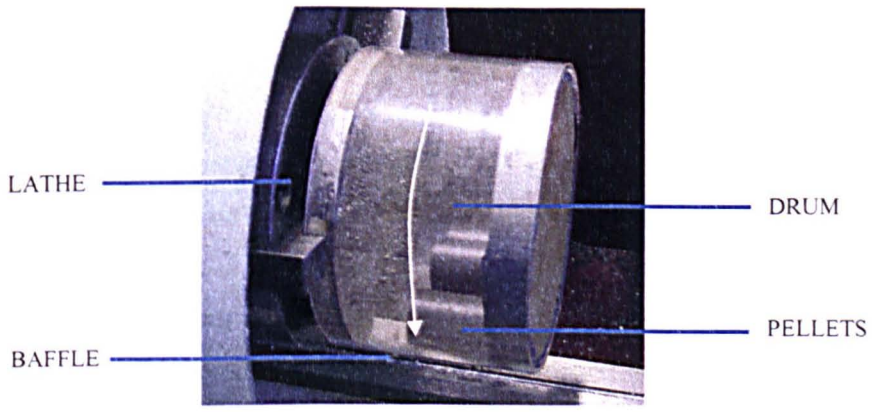


Figure 7.3: The drum with baffle, mounted on the lathe, used to test pellet durability.

This is based on the prototype testing method of Temmerman, *et al.* (2004, 2006), considered in Section 5.7.3. Whilst there are a range of other testing methods to determine pellet durability, based on the constraints concerning both the project scope (limitations on finances and timescale) and the materials (availability), this was the most suitable technique. Temmerman, *et al.* (2006) also explored standard tests, such as ASAE S269.4 and ÖNORM M 7135, considered in Section 5.7.3. In both cases, durability is expressed as the average percentage mass remaining of the total sample and therefore this was how the results herein were reported. The tests were also repeated for each case.

7.3.4 Experimental Measurement Accuracy and Error Analysis

The accuracy of the experimental readings was likely to be the main source of error in the data obtained from these tests. All data collection here will have had errors to some degree regarding the measurement of weight (± 0.05 g), time (± 0.5 s), pressure (± 5 psi), length (± 0.5 mm), compressive strength (± 5 N) and moisture content (± 0.25 %), all of which will have impacted the results. For the pelletisation work concerning the use of elevated temperatures, steam and binders, there would also be errors concerned with the experimental measurement of temperature (± 0.5 °C). The equations used herein may also include some inaccuracies, thus the inputting of erroneous data into these may have lead to additional inaccuracies in the values. Moreover, data that are rounded may further increase this error.

7.4 EXPERIMENTAL METHODOLOGIES: THE EFFECTS OF CHANGING THE PELLETISATION PARAMETERS

Various aspects of pelletisation theory were considered in Section 5.8, including the identification of many variables that can be manipulated to modify pellet properties and characteristics. These included the initial and final moisture contents, the maximum pressure obtained during pelletisation, the holding time at the maximum pressure and the pellet composition. These parameters and the methodologies used to examine their effects on pellet quality are explored here, the results of which are presented in the following section. From these data, optimum values for the pelletisation parameters could be established.

7.4.1 Effect of Moisture and Drying

Moisture content is a factor that significantly affects pellet properties, as previously demonstrated. The moisture content was experimentally determined using the method described in Section 6.2.1. The two studies here investigated the effect of moisture on the density and tensile strength of coal tailing briquettes, as the effect of moisture and its elimination after pelletisation can significantly affect such properties. For the first case, briquettes were made at room temperature (RT) from wet coal tailings as described above in Section 7.2, and according to Table 7.1 (Case 1); the pellet properties were then determined using the above methods when various degrees of drying occurred, from the initial moisture content to when the material was air-dried: from 16 % to 6 %. Based on the literature, the hypothesis was that the tensile strength of briquettes would increase on drying. The second case examined the effect of

drying the coal tailings prior to pelletisation rather than the briquettes after manufacture; here, briquettes were made from coal tailings with varying moisture from an initial moisture content of 17.3 %, to 0.82 % after complete air-drying, according to Table 7.1 (Case 2). Pellet properties were assessed immediately after briquetting. The hypothesis was that wet briquettes would have a lower tensile strength.

VARIABLE	CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6
Moisture (%)	★	★	2, 10	10	10	10
Pressure (psi)	2436	2436	★	2436	2436	2436
Holding Time (s)	20	20	20	★	20	20
Composition	coal tailings	coal tailings	coal tailings	coal tailings	★	★SMC

Table 7.1: The variables used for the different case studies. 2436 psi is equivalent to 16.8 MPa. ★ indicates the parameter manipulated.

7.4.2 Effect of Pressure

The pressure in the pelletiser was measured using the pressure gauge, thus it could be varied to quantify its effects on coal tailing briquette quality. The pressure used when forming a briquette was altered for eight different conditions, ranging from 812 psi to 7308 psi (5.6-50.4 MPa), keeping all other variables constant, as outlined in Table 7.1 (Case 3). An optimum pressure could therefore be suggested that provided a balance between the most suitable pellet properties and minimum cost, based on energy input and pressure used. The hypothesis here was that the tensile strength of the briquettes would increase as the maximum pressure increased, although there will be a limit, after which further energy inputs would not result in significant density or tensile strength improvements; the aim of this case study was to determine this limit, and thus the optimum pelletisation pressure. The pellets were made with two different moisture contents; some were approximately 10 % moisture, and the rest were thoroughly air-dried. The hypothesis for this was the same for the cases investigating the effect of moisture content.

7.4.3 Effect of Holding Time

The holding time was another factor that may influence briquette quality; it is also known to affect the density of pellets. In this experiment, briquettes were made according to Table 7.1 (Case 4) and the holding time at the maximum pressure was altered: from 5 seconds to one minute. From this, it was hoped that an optimal holding time could be determined. It was hypothesised that short holding times would result in reduced briquette density and tensile strengths; as holding time increased, the briquettes should become denser and have higher tensile strengths. It has previously been found that holding times over 20 seconds may have little further impact on briquette properties. From the literature, it was found that holding time is thought to be more significant at lower pressures.

7.4.4 Effect of Pellet Composition

These studies aimed to assess the quality of pellets formed using the optimum ratio of SMC to coal tailings and also using only SMC. The pellets in both cases were made according to Table 7.1. For the first part (Case 5), it was necessary to establish the ratio that gave the best possible pellet qualities. For

this, pellets were made of varying SMC:coal tailing ratios (from 0:100 to 100:0). Pellet dimensions were determined to quantify expansion after pelletisation. Secondly, two conditions were used to assess the role and effect of the casing layer and whether it should be included in the pellets: (i) pellets were made with a mixture of both SMC layers and (ii) pellets were made using only the substrate layer, where the casing was removed (Case 6).

7.5 RESULTS: EFFECT OF CHANGING THE PELLETISATION PARAMETERS

The above section detailed the conditions under which the pellets were made. Many variables in the pelletisation process were manipulated and these were investigated to ascertain the optimum pelletisation conditions. Five pellets were tested for each condition within the various cases and average results were taken to minimise errors. 95 % Confidence Limits are shown on the scatter plots; this was determined using the significance level (in this case 0.05), the standard deviation of the data and the sample size. The results gained herein were compared to those outlined in the literature discussed in Chapter 5. From the results of the pelletisation parameter assessment, the maximum pellet pile height was calculated for various cases and in addition to this, the durability of a range of pellets was determined.

When the pellets were tested for compressive strength using the Brazilian test, there were two ways in which the pellet could deform. The first was fracturing, where the pellet cracked or broke on reaching the maximum force it could withstand, as shown in Figure 7.2. The second was deformation of the cross-section; as these pellets had a circular cross-section, they became oval on deformation at high pressures if they were flexible. The coal tailing briquettes deformed by cracking or breaking, whereas those containing SMC deformed to an oval cross-section, as the fibres were more flexible than the finer particles of the coal tailings; these pellets remained intact due to the fibres which held the other particles together. This shows the impact of the inclusion of SMC into the pelletised mixture.

7.5.1 Effect of Moisture and Drying

Cases 1 and 2 concerned the effect of moisture on coal tailing briquette quality. Due to the compression of wet coal tailings during briquetting, moisture was expelled (Figure 7.4).

Figure 7.4: The expulsion of moisture during the pelletisation of wet coal tailings.

There were significant differences between briquettes at various stages of drying, demonstrating changes to their tensile strengths (Figure 7.5). Briquettes with high moisture contents had the lowest tensile strength and air-dried briquettes, with the lowest moisture content (~6 %), had significantly higher tensile strengths. This study showed drying is integral to forming briquettes of sufficient quality, as hypothesised; this concurs with the literature discussed (Daubert, 1973; Messman, 1977; Li and Liu, 2000; Radloff, *et al.*, 2004).

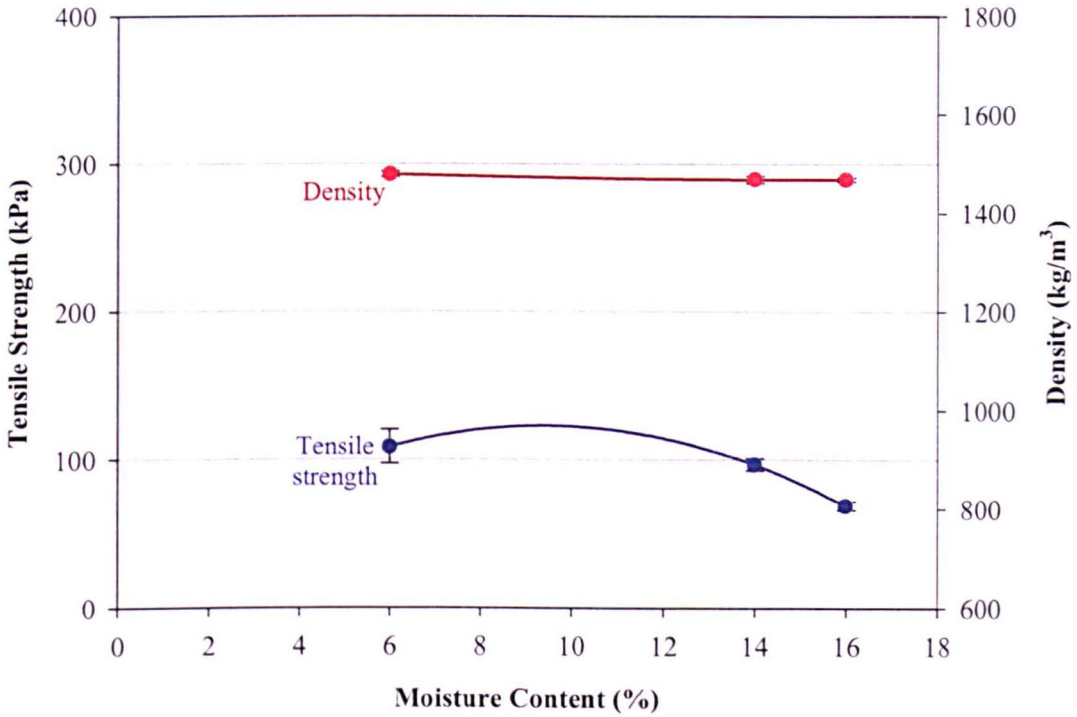
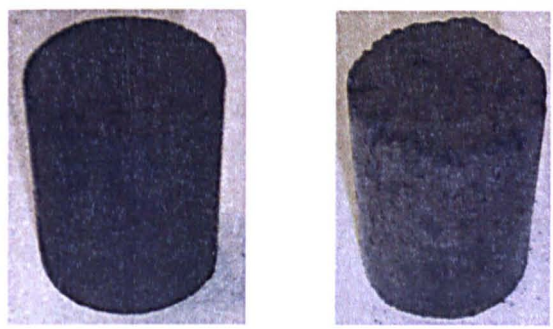


Figure 7.5: The effects of briquette moisture on tensile strength and density – Case 1.

For Case 2, there were physical differences between pellets made at different moisture contents (Figure 7.6). The wet coal tailing briquettes were dark grey-black with a dull surface, but became slightly lighter on drying (as seen in Case 1), whereas briquettes from air-dried coal tailings were shiny, due to friction with the mould that polished the surface, as discussed in Chapter 5.5.2. These briquettes were lighter in colour and crumbly, as this polishing action caused by friction between the material and the mould wastes energy which could have been used for compaction, thus the quality was severely reduced, shown below.



(a) (b)

Figure 7.6: Briquettes of: (a) wet – 10 % moisture; and (b) air-dried coal tailings – 2 % moisture.

As hypothesised, the wettest briquettes were weak, as the moisture prevents sufficient compaction; additionally, the driest ones were also weak, as the plasticity of particles was reduced by low moisture (Figure 7.7). This clearly shows the effect of initial briquette moisture. The optimum moisture content was 10-11 %. An appropriate moisture content at briquette formation followed by drying was vital – often the most influential factor, as found in many literary sources (Kleinebudde and Lindner, 1993; Li and Liu, 2000; Mani, *et al.*, 2006). The density decreased as moisture was removed from the pellets, and there was little variation in the density for each condition.

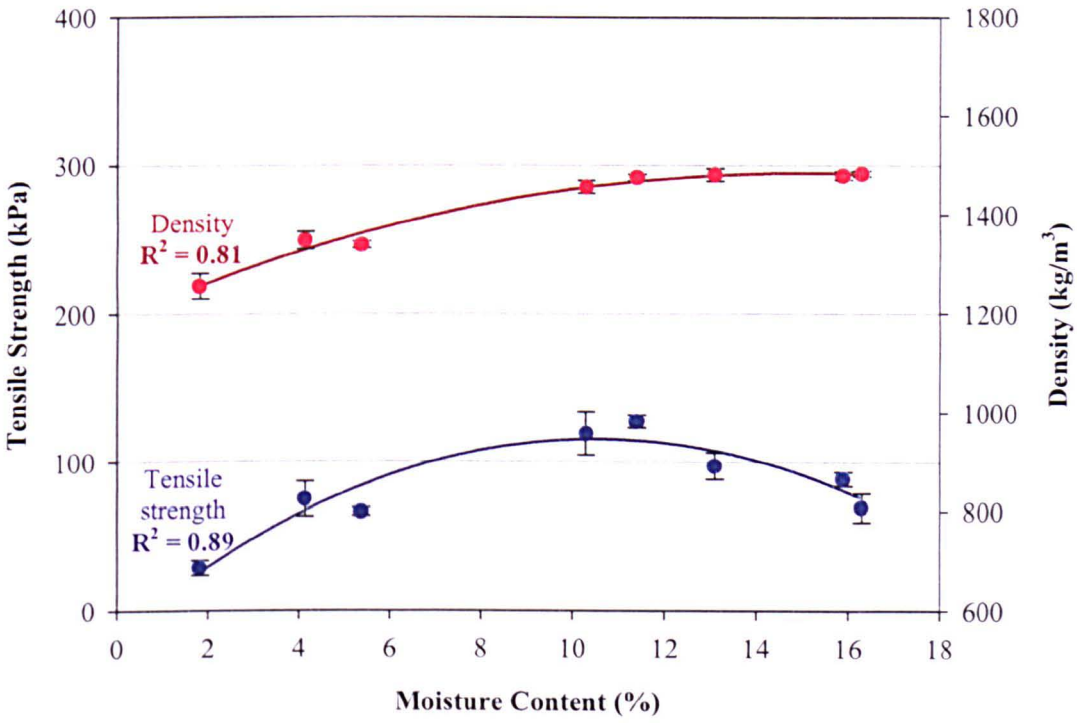


Figure 7.7: The effects of briquette moisture on tensile strength and density – Case 2.

7.5.2 Effect of Pressure

Coal tailing briquettes were formed at two different moisture contents (2.24 and 9.15 %) and a range of different pressures; the results for these tests are shown in Figure 7.8. There was a very strong correlation between the tensile strength and compaction pressure, as shown by the R^2 values. As hypothesised, there does become a point, however, when the increase in tensile strength is minimal compared to the increase in pressure. This was approximately 6000 psi (41 MPa) for the drier briquettes; this is still classed as low pressure pelletisation (Rieschel, 1963). At this point, the energy and cost of producing a significantly higher pressure would result in a fairly small improvement in the tensile strength, and thus using pressures above this would not be economical. Furthermore, there was also a clear trend between density and pressure. Increasing the briquetting pressure ensured greater densities for both moisture contents.

There was also a strong relationship between pellet density and tensile strength (Figure 7.9), as the binding was likely to be stronger when particles were forced closer together. This may be influenced by the particles' plasticity, particularly if the materials were pelletised at their optimum moisture content,

thus there were differences in the relationships for varying moistures, indicating a different association. For low moistures, the trend appeared linear, whereas for the higher moisture content pellets the trend was polynomial order 2, though the significance of the correlations were similar and strong, as shown by the high R^2 values on Figure 7.9. This showed a distinct and strong relationship between the variables, where the ideal pressure can significantly improve briquette quality, as considered by Rieschel (1963), Li and Liu (2000), Lehtikangas (2001), Obernberger and Thek (2004) and Rhén, *et al.* (2005) among others; this optimal pressure is where a balance of briquette quality and cost (based on energy expenditure) is achieved. Lower pressures could be used with the application of a suitable binder.

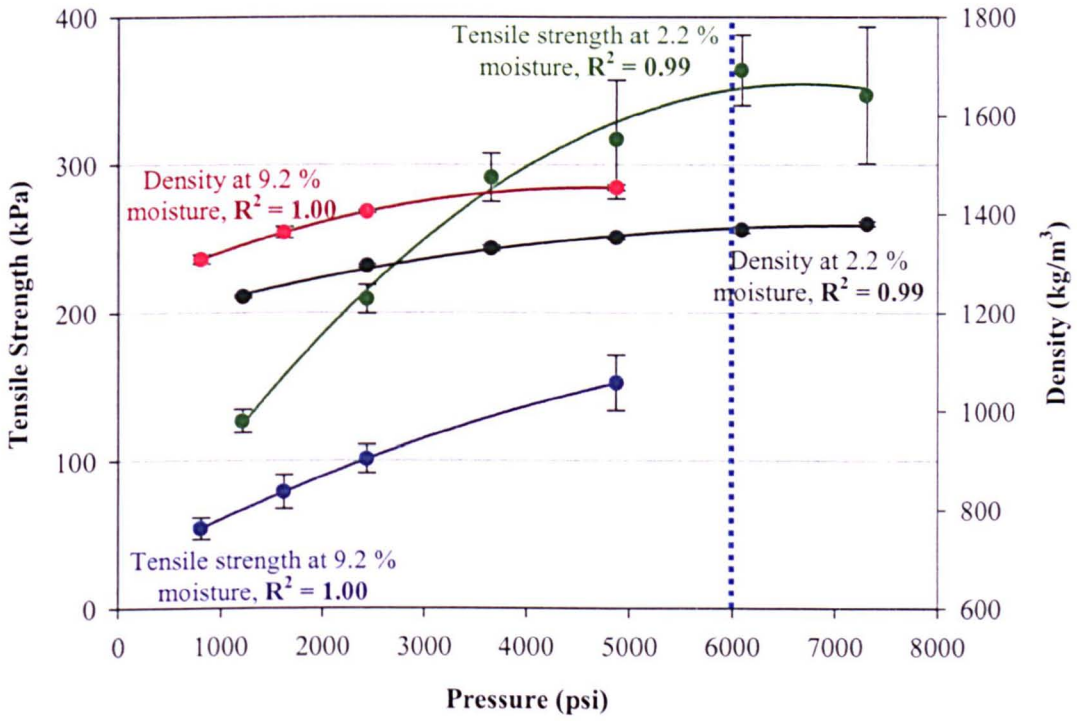


Figure 7.8: The effects of pressure on tensile strength and density – Case 3.

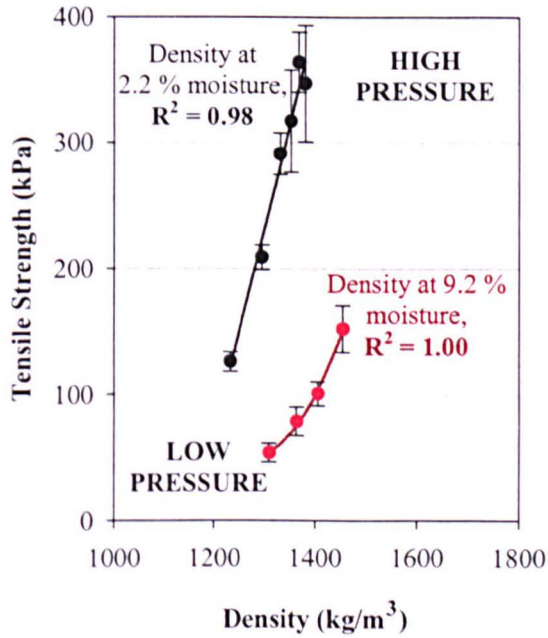


Figure 7.9: Relating the tensile strength and density of coal tailing briquettes made at varying pressures.

7.5.3 Effect of Holding Time

Fifteen coal tailing pellets were made according to the briquetting conditions outlined in Table 7.1. The results, presented in Figure 7.10, show the expected relationship between holding time and density, where as holding time lengthens the density of the briquettes increase; this is, however, a fairly negligible effect, with only small increases in density. The relationship between the tensile strength and the holding time is less obvious, but the increase in strength at lower holding times may be affected by compaction speeds, which could be faster here. The results from Case 4 were not as significant as the literature suggests for other pelletised substances, and therefore this variable is not considered as important as those above (Jones, 1969; Li and Liu, 2000).

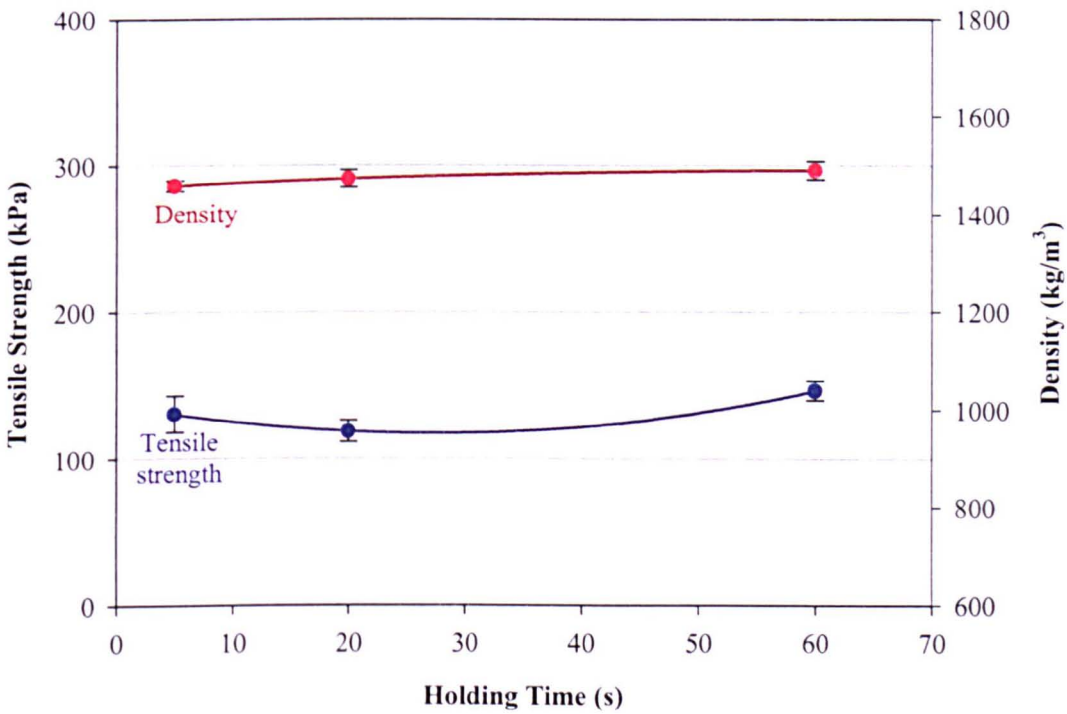


Figure 7.10: The effect of holding time on tensile strength and density – Case 4.

7.5.4 Effect of Pellet Composition

This section aimed to establish the optimum ratio of SMC and coal tailings based on the tensile strength of the pellets formed. For this case study, the biofuel pellets were made according to the conditions outlined in Table 7.1 and Section 7.4.4 above; these pellets of various SMC-to-coal tailing ratios were dried and tested for tensile strength. Figure 7.11 represents this data graphically. The trend for the tensile strength of the pellets shows a distinct curve with a strong correlation. At low and high percentages of SMC, the tensile strength was low; the optimum ratio of SMC-to-coal tailings based on the tensile strength is about 50:50 wt%. As shown by the confidence limits for this case, the variation in tensile strength increases with variation of its content. The pliability of the pellets is enhanced by the additions of SMC, which makes them far more able to withstand higher pressures, probably brought about by the flexibility of the fibres and the coal tailings' ability to bind to these.

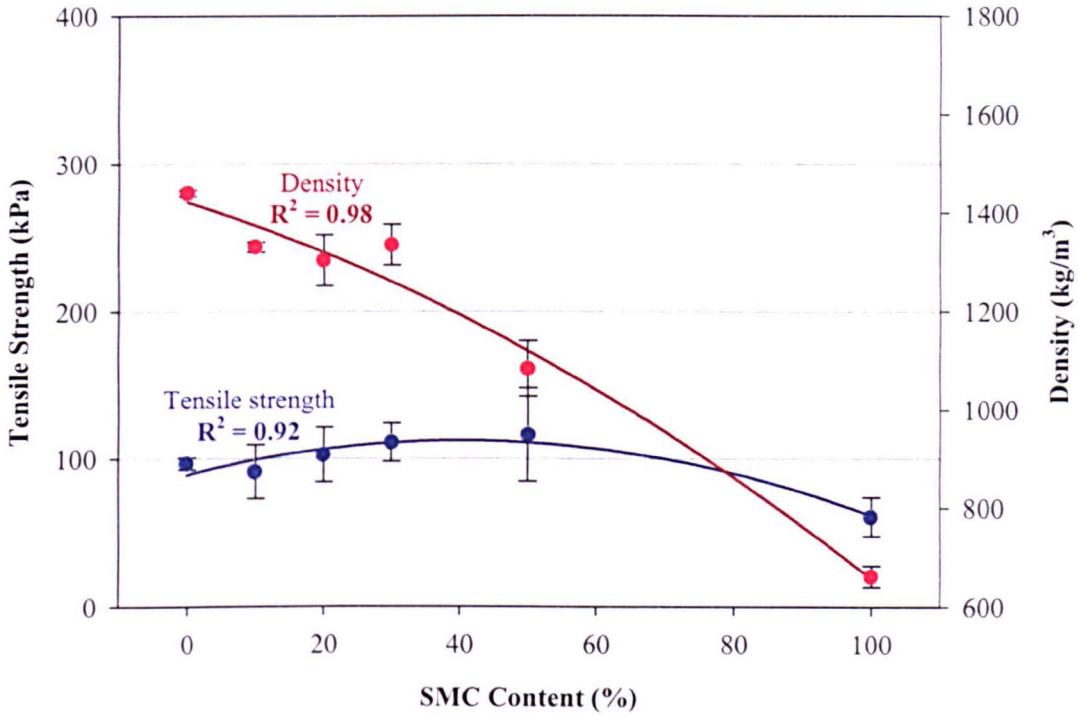


Figure 7.11: The effect of the SMC-coal tailing ratio on tensile strength and density – Case 5.

Furthermore, all the pellets containing SMC, no matter what their composition, expanded to some extent after pelletisation and cracks were clearly visible (Figure 7.12). As these cracks were already present in the structure prior to testing, the pellets were able to withstand greater tensile strengths before they broke further. Deformation of the structure did occur where particularly high tensile strengths were reached, although the pellets remained coherent. As the proportion of SMC increases, however, there were considerable density changes. The pellets also lengthened with increasing amounts of SMC and thus their density decreased, as shown.

Figure 7.12: Fuel pellets of various SMC:coal tailing ratios: left – 50:50 wt% ratio, centre – 20:80 wt% and right – 30:70 wt%.

Pellets of the SMC and SMC substrate were also compared and were made according to Table 7.1 and their density and tensile strength were measured after air-drying. The results for these two test conditions are shown in Figure 7.13. As can be seen, the tensile strength of the pellets containing only the SMC substrate was significantly greater, as were their densities; the 95 % confidence limits, however, show that there was also greater variation for these pellets than those with the casing layer included.

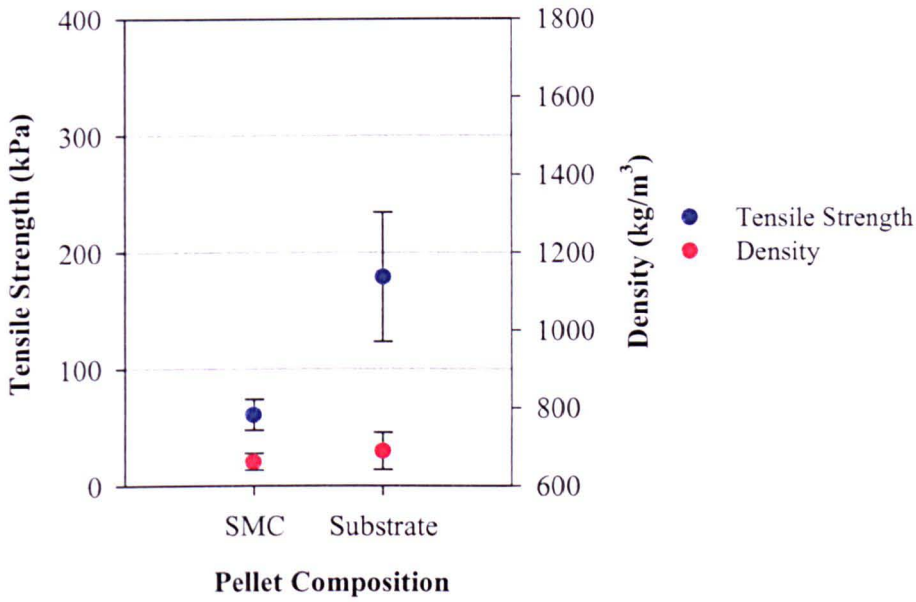


Figure 7.13: The tensile strengths and densities of SMC and SMC substrate pellets – Case 6.

The material characterisation also aided the evaluation of the inclusion of the casing layer in the pellets, particularly the assessments of the CV and ash content. This, coupled with the results from Case 6, suggests that the inclusion of the casing layer does not enhance pellet properties and therefore the removal of this should be considered for the final pellets, if possible. The casing layer does not appear to provide any form of additional binding, whereas the coal tailings could perform this function. Furthermore, the CV of the casing is lower than for the other components and the ash content is also high; thus, there are many reasons why the inclusion of this casing layer may be detrimental to a number of pellet qualities. Although the removal of the casing layer has its advantages, there are also several reasons why its inclusion is necessary; it is not easy to separate the two SMC layers and therefore contamination of the substrate may occur. Additionally, the removal of this layer will mean it requires disposal. Consequently, the casing layer is likely to remain in the pellets and the properties will hopefully be improved by the additions of coal tailings, which enhances the CV.

7.5.5 Overall Comparison of Pellet Pile-Up Studies and Durability

As a variety of SMC, coal tailing and SMC-coal tailing pellets had been manufactured in the above cases, several were selected for pellet pile-up calculations and durability testing, performed using the methods described in Sections 7.3.2 and 7.3.3. For the pellet pile-up studies, previously determined data was utilised to determine the maximum height of pellet piles, computed by employing Equations 7.2-7.5. Table 7.2 shows the various heights of the piles for different pellets, which compares: 1 = pellets made with the optimum moisture content and SMC:coal tailing ratio; 2 = pellets made using the optimum moisture and pressure; 3 = wet pellets; 4 = air-dried pellets; 5 = SMC only pellets; and 6 = SMC substrate only pellets. Of these, high pressure coal tailing pellets and the substrate only pellets (2 and 6) could withstand the greatest height, in excess of 30 m; the optimum pellets were better than the other cases considered, particularly cases 3 and 4, where only coal tailings was used.

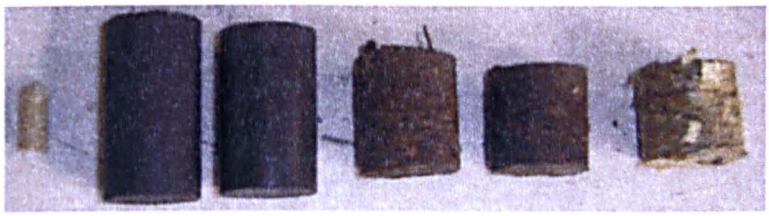
VARIABLES AND PARAMETERS	1	2	3	4	5	6
Initial Moisture Content (%)	10.5	~10	16.3	16.0	~15	~15
Drying	yes	yes	no	yes	yes	yes
Pressure (psi)	2700	6000	2700	2700	2700	2700
Composition (SMC:Coal Tailings)	50:50	0:100	0:100	0:100	100:0	substrate
***L*, Pellet Length (mm)**	43.0	43.2	31.8	32.0	56.7	57.7
ρ_P, Density (kg/m^3)	1083.7	1367.9	1483.3	1371.0	661.4	689.7
Compressive Strength (kPa)	134.3	421.7	59.1	93.2	92.5	277.1
W, Weight (kg)	11.9	43.0	7.1	9.5	9.4	28.3
Weight/Pellet (kg)	0.026	0.033	0.027	0.025	0.021	0.022
$P_{no.}$, Number of Pellets	451.7	1290.4	266.1	384.4	445.9	1258.7
H_P, HEIGHT OF PELLET PILE (m)	**12.10**	**34.58**	**7.13**	**10.30**	**11.95**	**33.73**

Table 7.2: Results for the maximum heights of various types of pellet piles.

The durability of a selection of pellets made under various conditions was determined using the rotating cylinder shown in Figure 7.3. From some preliminary experimentation using the drum, it was found that the pellets did not rotate and were therefore not subjected to mechanical shock; they simply sat in the bottom of the cylinder and were gradually abraded. Due to this, a small baffle was added to increase the quantity and magnitude of mechanical shocks experienced by the pellets, although abrasion was still seen to some extent. The results of these tests are shown in Table 7.3. 50:50 SMC-coal tailing pellets were reasonably durable, where about 30 % mass was removed after 20 mins in the drum. Other pellets were tested for comparison and included straw pellets using the pelletiser described above and commercially produced extruded wood pellets (Figure 7.14), which were both highly durable, losing less than 2 % of their mass after 10 mins. The most durable pellets from this test were ones made from SMC, where those produced at higher pressures were more durable, where other pelletisation variables were kept the same.

MATERIAL	PELLETISATION CONDITIONS	DURABILITY: % MASS REMAINING
Straw	dry, 2440 psi (16.8 MPa)	98.88
Wood	extruded	98.83
SMC	dry, 4870 psi (33.6 MPa)	98.28
SMC	dry, 2440 psi (16.8 MPa)	92.96
Coal Tailings	wet, 2440 psi (16.8 MPa)	88.18
Coal Tailings	dry, 2440 psi (16.8 MPa)	79.71
20% SMC	2440 psi (16.8 MPa)	79.13
Coal Tailings	dry, 4870 psi (33.6 MPa)	75.93
50% SMC	2440 psi (16.8 MPa)	71.14
Coal Tailings	dry, 1220 psi (8.4 MPa)	66.75

Table 7.3: The effects of pellet composition and pelletisation conditions on durability.



(a) (b) (c) (d) (e) (f)

Figure 7.14: A selection of pellets used for durability tests; (a) extruded wood pellet; (b) coal tailing briquette at 2440 psi (16.8 MPa); (c) coal tailing briquette at 4870 psi (33.6 MPa); (d) an SMC pellet at 2440 psi; (e) SMC pellet at 4870 psi and (f) straw pellet.

7.5.6 Optimum Values for the Pelletisation Variables Tested

From the above tests, optimum values can be determined for each pelletisation variable, upon which further examinations into pellet quality can be based. Optimum pellets can be manufactured by employing the most ideal conditions for each of the following variables: initial moisture; degree of drying; maximum pressure achieved during compression; and SMC-coal tailing ratio. The holding time was shown not to be as influential for these materials as others considered in the literature.

Pellets made from either wet or dry materials had low tensile strengths; if wet pellets were air-dried, they became significantly stronger, withstanding much greater forces (tensile strengths up to 125 kPa) and were more durable than those that were still moist. An initial moisture of 10-11 % followed by air drying appears optimal for these pellets. Pressure was also an important influence on pellet quality. At least 2500 psi (17.2 MPa) was needed for pellets to be of significant quality (tensile strengths over 100 kPa). Greater pressures, up to 6000 psi (up to 41.4 MPa), resulted in much stronger pellets (tensile strength of 350 kPa), although this would also require much greater energy inputs. The optimum SMC:coal tailing ratio was determined to be 50:50 wt%, as the intertwined fibres in the SMC substrate provided flexibility within a matrix of the SMC casing layer and coal tailing particles. The addition of the fibres to the coal tailing pellets was beneficial in that it allowed deformation rather than breakage of the pellets when under pressure, thus they remained in tact. Pellets of mainly SMC or coal tailings were weaker by comparison (60 and 95 kPa respectively compared to 115 kPa). Durability tests showed that pellets formed at high pressures and then air-dried were most durable. Whilst pellets with improved characteristics could be produced by optimising the pelletisation process, the product was still found to generate dust on handling, thus ways in which pellet quality could be further improved were required. A variety of methods were assessed, comprising the inclusion of binders, additions of steam (conditioning the materials prior to pelletisation) and pelletisation at elevated temperatures, which were also considered in Chapter 5.

7.6 EXPERIMENTAL METHODOLOGIES: THE EFFECT OF BINDING AGENTS ON PELLETISATION

As stated above, pellet composition is a key influence on pellet properties; this includes the addition of a binder. Particle agglomeration mechanisms and the use of binders were discussed in Section 5.5. This section considers the impacts on pellet quality for the addition of two binders – caustic soda and starch.

7.6.1 Review and Selection of Binders

7.6.1.1 Inorganic Binder: Caustic Soda

Caustic soda (CAS 1310-73-2) – also known as anhydrous sodium hydroxide or NaOH – was the first binding agent to be identified for the pelletisation of SMC and coal tailings. This inorganic alkali binder is thought to be both cost-effective and efficient in performing this function (Yoo and Jo, 2003). Some literature reports the results of pelletisation tests which include the use of NaOH, although only one is

specifically related to fuel pelletisation. Zhang, *et al.* (2001) examined a range of biomass treatments to form a binder for lignite briquettes, as considered in Section 5.9.3 and depicted in Figure 5.15. McManus, *et al.* (1975) used different alkalis (NaOH and KOH) to treat roughages that are fed to sheep; although the primary aim was to improve the nutrient value of the feed pellets, significant improvements in pellet quality were also noted, namely pellet hardness. It was initially found that ground Lucerne treated with the alkalis (0, 3 or 6 %) during pelletisation formed harder pellets. Furthermore, additional experiments discovered that rice hulls treated with differing amounts of NaOH spray and then pelletised with untreated ground Lucerne became increasingly hard, proportional to the amount of NaOH used. Yoo and Jo (2003) have also tested NaOH as a binder. The strength of flyash pellets was improved with additions of both alkali and acidic binders, including NaOH, particularly when sintered at high temperatures; such binders were also found to be economic. A range of organic (methyl cellulose and polyvinyl alcohol) and inorganic (lime and cement) binders were also tested, but were not practical.

7.6.1.2 Organic Binder: Starch

Starch, $(C_6H_{10}O_5)_x$, was the second binder (CAS 9005-25-8). This is an organic material, the molecular structure of which is shown in Figure 7.15. It is often used as a biological binding agent for a variety of purposes; it has pharmaceutical applications, as well as uses in fuel and animal feed pelletisation, many of which are considered below. Other applications of starch in a binding context involve its use in laser-induced breakdown spectroscopy, due to the role of matrix effects (Gondal, *et al.*, 2007).

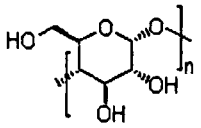


Figure 7.15: The molecular structure of a starch monomer $(C_6H_{10}O_5)_n$ that link together, forming the starch polymer chain.
Source: chemBlink (2008)

Thomas and van der Poel (1996) and Thomas, *et al.* (1997; 1998) considered the physical quality of pelletised animal feed, based on hardness and durability, where starch was used as a binder. The binding was thought to be due to the solubilisation and crystallisation of components, such as starch, but also fats and sugars. It was found that the gelatinisation of the tapioca starch is one of the functional causative factors affecting pellet quality; this gelatinisation was caused by the physico-chemical changes by additions of heat and/or water, which enhanced the binding, subsequently leading to improved pellet quality. It was also seen that raw protein enhanced pellets, yet fats did not. In addition to these studies, starch has also been considered as a binder in the context of fuel pelletisation, for both coal and biomass. Burchill, *et al.* (1994) used molasses and modified starch to briquette coal; combined with ^{13}C nuclear magnetic resonance spectroscopy, favourable curing regimes were acquired to enhance briquette properties. Mehta and Parekh (1996) found that a suitable binder was needed to make the pelletisation of ultra-fine clean coal economical. Asphalt emulsion, corn starch and Brewax were investigated for this purpose. Asphalt emulsion and starch were not effective, although the Brewax produced pellets that were

acceptable, according to the minimum quality requirements. Tabil, *et al.* (1997) evaluated the performance of different binders, with the aim of improving the quality of alfalfa pellets, to reduce the production of dust during transportation and handling. A range of binders were compared: lignosulfonate, bentonite, pea starch, collagen protein and hydrated lime. All enhanced the durability and hardness of low-quality chop, but did not improve the durability of the medium or high quality alfalfa. Further testing revealed that just 0.5 % of pea starch or hydrated lime could increase pellet durability.

More recently, Obernberger and Thek (2004) tested various densified biomass fuels (pellets for combustion) from across Europe, to investigate pellet quality and European standards for pellet production in this context. The pellet parameters that were analysed included dimensions, density, ash content, CV, ultimate analysis and the determination of heavy metals; additionally, the starch content was established to provide an indication of the inclusion of biological binding agents during pellet production. The average starch content for dry wood pellets was found to be 0.22 wt%, where the maximum was determined to be 1.25 wt%. The starch was included to aid binding of the particles, to obtain higher abrasion resistance and to reduce the cost of pelletisation. They concluded that biological binders such as starch need only be used in small quantities (up to 2 wt%) in the production of fuel pellets. Jannasch, *et al.* (n.d.) state that starch could be utilised to improve biofuel pellet quality at a 'modest' cost.

7.6.2 Experimental Conditions

The literature above shows only a small percentage of both caustic soda and starch are required to impact pellet quality, which was assessed here. SMC-coal tailing pellets were made according to the optimum pelletisation conditions for these wastes outlined in Section 7.5.6, at 6000 psi (41.4 MPa). Seven different conditions were tested; the first was the control, where no binder was added. Additional pellets were made with varying quantities of the two binders: 0.5, 1 and 2 wt% of either the caustic soda or starch. The density, tensile strength and durability were evaluated and pellet pile-up studies determined the weight withstanding ability for each, as described above.

The caustic soda was in pellet form and required crushing prior to being mixed with the fuels. It had a minimum purity of 97.5 %, with small amounts of potassium (0.1 %) and carbonate (2 %) impurities. Care must be taken when handling NaOH, particularly when it comes into contact with moisture, due to its corrosive nature. It is thus classed as a hazardous chemical (Health and Safety Executive, 2008). A powdered maize-based starch was used here. Initially in powder form, it was mixed with a small amount of water to form a paste before being thoroughly incorporated into the SMC-coal tailing mixture.

7.7 RESULTS: THE EFFECT OF BINDERS ON PELLETISATION

Up to 1 wt% of both binders improved the tensile strength, but further additions weakened the pellets (Figure 7.16). Although opposite trends are seen for the density in both cases, the 95 % Confidence Limits overlap, suggesting that there is likely to be little statistical difference between the results.

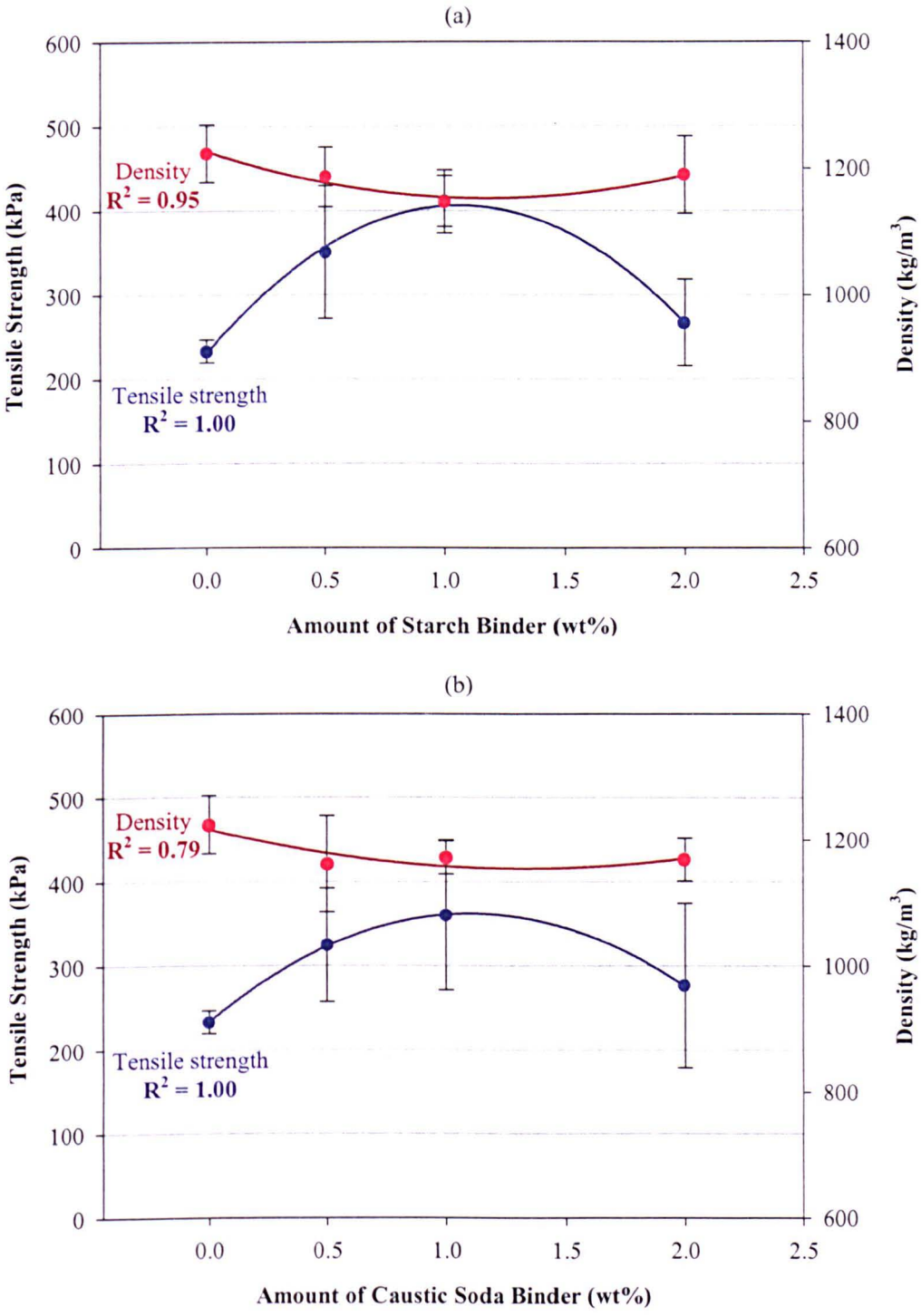


Figure 7.16: Graphs showing the impacts on the tensile strength and density of SMC-coal tailing pellets for (a) the starch binder and (b) the caustic soda binder. 95 % Confidence Limits are shown as error bars.

The caustic soda should be able to bond to the materials to aid agglomeration and improve pellet quality, however, as seen, this was not as effective as the starch binder (Zhang, *et al.*, 2001). Starch, which appeared better able to provide this binding function and increased the tensile strength more so than the caustic soda, was thought to assist particle cohesion by solubilisation and crystallisation within the pellet, in addition to physico-chemical changes through additions of water (~ 5 ml addition per 1.25 g of starch used here) and/or heat, which is considered below (Thomas and van der Poel, 1996; Thomas, *et al.*, 1997, 1998). As seen from the 95 % Confidence Limits in Figure 7.16, there were noteworthy variations in the

results, due to the lack of homogeneity in the materials. Consequently, single factor ANOVA tests were used to assess the significance in the differences between the conditions; 0, 0.5 and 1.0 wt % of the binders were compared. The only significant difference was found to be for tensile strength, using 0 and 1.0 wt% of starch. Using only a small amount of these binders is beneficial, as quality can be dramatically improved with minimal costs, making these binders economical.

Pellet pile heights were then established (Table 7.4). Both binders could be used to improve the pellet properties and increase the heights of pellet piles. Larger improvements were noted with additions of the starch binder, compared to the caustic soda. The height of the pellet pile could be increased, almost doubled using 1 wt% of starch, without damaging those at the bottom. Based on these results, the optimum percentage of each binder (1 wt%) was chosen and pellets were made to assess their durability. Pellets made with caustic soda were the most durable (with 40.4 % mass remaining after 20 mins), whereas starch slightly decreased the durability of pellets (31.9 %) compared to those without a binder (32.8 %). Pellet durability with the addition of a binder is considered further below.

VARIABLES AND PARAMETERS	BINDER (%)						
	None	Caustic Soda			Starch		
	0.00	0.50	1.00	2.00	0.50	1.00	2.00
Pressure (psi)	6000	6000	6000	6000	6000	6000	6000
Pellet Length (mm)	33.8	38.7	38.6	39.4	36.4	37.6	36.5
Density (kg/m^3)	1224	1162	1172	1169	1187	1148	1190
Compressive Strength (N)	332	531	587	461	540	650	407
Weight (kg)	33.9	54.2	59.9	47.0	55.1	66.3	41.5
Number of Pellets	1449	2139	2347	1811	2262	2725	1693
Height of Pellet Pile (m)	**38.85**	**57.33**	**62.92**	**48.55**	**60.62**	**73.05**	**45.39**

Table 7.4: The maximum heights of 50:50 SMC-coal tailing pellet piles using caustic soda and starch binders. 6000 psi is 41.4 MPa.

7.8 EXPERIMENTAL METHODOLOGIES: EFFECT OF STEAM AND ELEVATED TEMPERATURES ON PELLETISATION

As steam and elevated temperatures are often used to aid the agglomeration of particles during pelletisation, these were therefore the focus of additional research, presented here. A thorough examination of the effects of pelletisation at elevated temperatures on the quality of SMC-coal tailing pellets was conducted, along with the steam conditioning of these two wastes to further improve the quality of pellets. The primary aim of this was to evaluate a range of temperatures and varying amounts of steam additions prior to pelletisation and the impacts of these on pellet quality.

7.8.1 Use of Elevated Temperatures

The effect of temperature is often an important factor in pelletisation. Elevating the temperature may facilitate the agglomeration of particles, especially if a heat-softening binder has been applied or is inherent to the substance (Moore, 1965). Moreover, high temperature pelletisation is preferred for certain materials, particularly if a binder is not used. This was considered in more detail in Section 5.8.1.3.

7.8.2 Use of Steam

Steam pelletisation is where steam is introduced to the materials prior to compression or extrusion to condition the material. When steam pelletisation is an option, there are three main factors that need to be considered: (i) that an adequate volume/quantity of steam can be supplied; (ii) that the steam can be delivered at a controlled pressure; and (iii) that the water introduced with the steam can be suitably removed (Robinson, 1971). The first of these factors means that the size of the boiler needs to be determined, which is dependent on the feedrate of the feedstock and the moisture that is to be added during steam conditioning. Robinson (1971) states that, in general, high-pressure boilers are preferred to low-pressure systems, particularly for pellet mills, as different steam pressures can be produced, based on the material characteristics and furthermore, smaller equipment can be installed.

Various studies have investigated this use of steam, with the principal aim of enhancing pellet quality; this has been considered in the context of fuel pellets and animal feeds. For fuel pelletisation, this mainly concerned biomass, where steam can soften components, such as lignin or cellulose, and enhance their flexibility, as with elevated temperature. This in turn aids particle agglomeration and binding, improving pellet quality. Furthermore, steam can act as a lubricant to ease pelletisation. Dry or wet steam can be utilised for this purpose, depending on the moisture required for pelletisation. Jannasch, *et al.* (n.d.) studied how the binding quality and durability of switchgrass biofuel pellets could be improved using high-temperature steam to activate natural binders within the biomass and aid lubrication. This decreased energy consumption. It was also found that although water had similar effects, it was less pronounced than for steam. Lehtikangas (2000) also investigated the additions of steam to sawdust, logging residues and bark pellets. Good quality pellets could be formed using high-temperature steam pre-treatment and long holding times at high pressures. This achieved the maximum softening of biomass components, which resulted in excellent agglomeration. Alakangas and Paju (2002) considered the effect of additives on wood pellets. They state that steam is the most general additive for pelletisation applications, either in dry or superheated form, added to the raw feed material in the mixing chamber to add heat without excess moisture. This heats and softens the lignin present in the wood, which may melt and help bind the particles, leading to a stronger, tougher product and reduced wear on the mould.

Briefly examining this for animal feeds, Skoch, *et al.* (1981, 1983) investigated the impacts of steam conditioning for pelleted poultry and pig feeds. It was found in both instances that additions of steam prior to pelletisation improved durability during transportation and handling. The steam did not damage the starch present in the material, which is beneficial, as this is also known to enhance agglomeration. Additionally, steam significantly increased the production rates. The decrease in mechanical friction between the mould and feed material was brought about by the lubrication effect of the steam, which meant that electricity consumption during pelletisation was reduced. However, the overall energy consumption increased by approximately 17 %, with more noteworthy increases as the steam temperature was raised. Robinson (1971) also discusses similar advantages of the steam pelletisation of animal feeds;

these included increased production, reduced wear to the mould and improved pellet quality, in terms of strength and breakage. Cutlip, *et al.* (2008) found that the pellet quality of broiler feed was improved using high temperature (82.2-93.3 °C) and pressure (138-552 kPa) steam.

The use of steam to improve pellet quality has been used with great success for a range of applications by activating the natural (inherent) binders, such as lignin, in the variety of biomasses that are pelletised in this way. It often leads to an overall cost increase however; Thek and Obernberger (2004) considered the implications of steam conditioning on the cost of wood pellet production, concluding that a 4 wt% addition of steam incurred a small increase in costs compared to the total for pelletising this material.

7.8.3 Experimental Conditions

As SMC is composed primarily of straw, lignin could be present, which may soften and act as a binder at elevated temperatures. Two 250 W rope heaters (OMEGA FGR-060) surround the vertical shaft of the mechanical pelletiser and were set to a specific temperature, using a control gauge (Figure 7.1). Pelletisation of SMC and 50:50 wt% SMC:coal tailing mixtures at room temperature, RT (15-20 °C), was compared to four elevated temperatures, ranging from 45 °C to 125 °C, at 6000 psi (41.4 MPa), to assess the effects on pellet quality. Pellets were made with a slightly higher moisture content (~15 % compared to 10-11 %) to mitigate the effect of drying caused by the heating of the material. The modifications to pellet quality were established by determining the density, tensile strength and durability, and comparing the pellet pile-up results, as before. The literature in Section 7.6.1 also described how the use of elevated temperatures coupled with a binder could further enhance pellet properties and improve their quality. For these reasons, pelletisation of the SMC-coal tailing mixture with 1 wt% of each binder was undertaken at the optimum temperature determined from this study.

Since the pelletisation of biofuels and other biomasses with steam additions has proved to enhance pellet quality, as described above, equipment that can inject super-heated steam into the feed material was developed. A 200 mm-diameter stainless steel conditioning chamber was constructed, to which a steam generator (Electrolux Z350A Enviro Steam Gun) was connected. This produced steam at 120 °C and around 2.5 bar (250 kPa), with maximum steam production at 45 gr/min. The conditioning chamber was pre-heated to ensure that the steam produced from the generator did not condense onto the surfaces. The pelletiser chamber was also heated to further ensure minimum condensation. These components are pictured in Figure 7.17. The steam temperature used here was greater than those used by Cutlip, *et al.* (2008), although the pressure was similar.

The SMC and coal tailings were dried to approximately 5 % moisture and then mixed thoroughly in a 50:50 wt% ratio. Six SMC-coal tailing samples were conditioned for varying lengths of time, ranging from 2.5 mins (150 s) to 10 minutes (600 s). After this, the material was transferred to the pelletisation rig, the chamber of which was heated to ensure that the material was not cooled and the moisture

condensed. The material was then pelletised according to the optimum conditions outlined above, followed by complete air-drying to remove the moisture added during steam conditioning. Pellets were also analysed where no steam conditioning had taken place. Pellet quality was assessed as above.

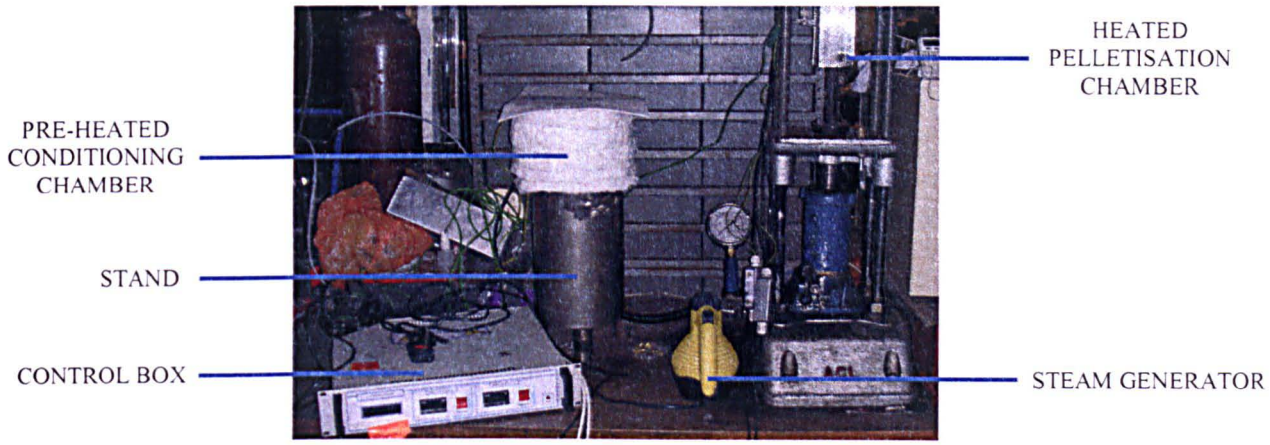


Figure 7.17: Experimental set-up for the steam conditioning chamber and pelletisation rig.

7.9 RESULTS: EFFECT OF ELEVATED TEMPERATURES AND STEAM ON PELLETISATION

7.9.1 Effect of Pelletisation at Elevated Temperatures

Pellets made at a range of elevated temperatures were compared to those made under the same conditions at room temperature (15-20 °C). As seen on Figure 7.18, pellet quality was improved in terms of density and tensile strength with temperature elevations. This was true for both pellet compositions, although was more pronounced for the SMC, as the largest improvements were seen here. As explored above, it is thought that the lignin and cellulose present in the biomass – in this case, the straw component of the SMC substrate – softens to aid the agglomeration of particles by filling void spaces within the densified pellet, which then cools and solidifies. This is thought to be similar to the effects of the tar-binding mechanism during the pelletisation of coals at elevated temperatures (Jones, 1969). Based on these results, the optimum pelletisation temperature is around 75 °C, although vast improvements were seen at just 45 °C, particularly for the SMC, as there would be a larger proportion of lignin and cellulose present. Additional temperature increases (up to 125 °C) appeared to be detrimental to pellet quality.

The Confidence Limits on Figure 7.18 show the variation in the results was large, particularly for the tensile strengths of the SMC pellets, although the averages suggest sizeable differences between the temperatures tested; this variation is primarily due to the heterogeneity of the materials. As such, ANOVA tests were completed to assess the statistical differences between the improvements in densities and tensile strengths of pellets made at RT, 45 °C and 75 °C. Despite the apparent large variation in results, particularly in the tensile strengths, the ANOVA tests indicated there were statistically-significant differences between the densities and tensile strengths of SMC pellets made at RT and 45 °C, and also between those made at RT and 75 °C. No difference was found however between those made at 45 °C

and 75 °C, indicating that 45 °C could be used to similar effect, but with incurring fewer costs. The results for SMC-coal tailing pellets showed no statistical differences in the densities or tensile strengths at any temperatures.

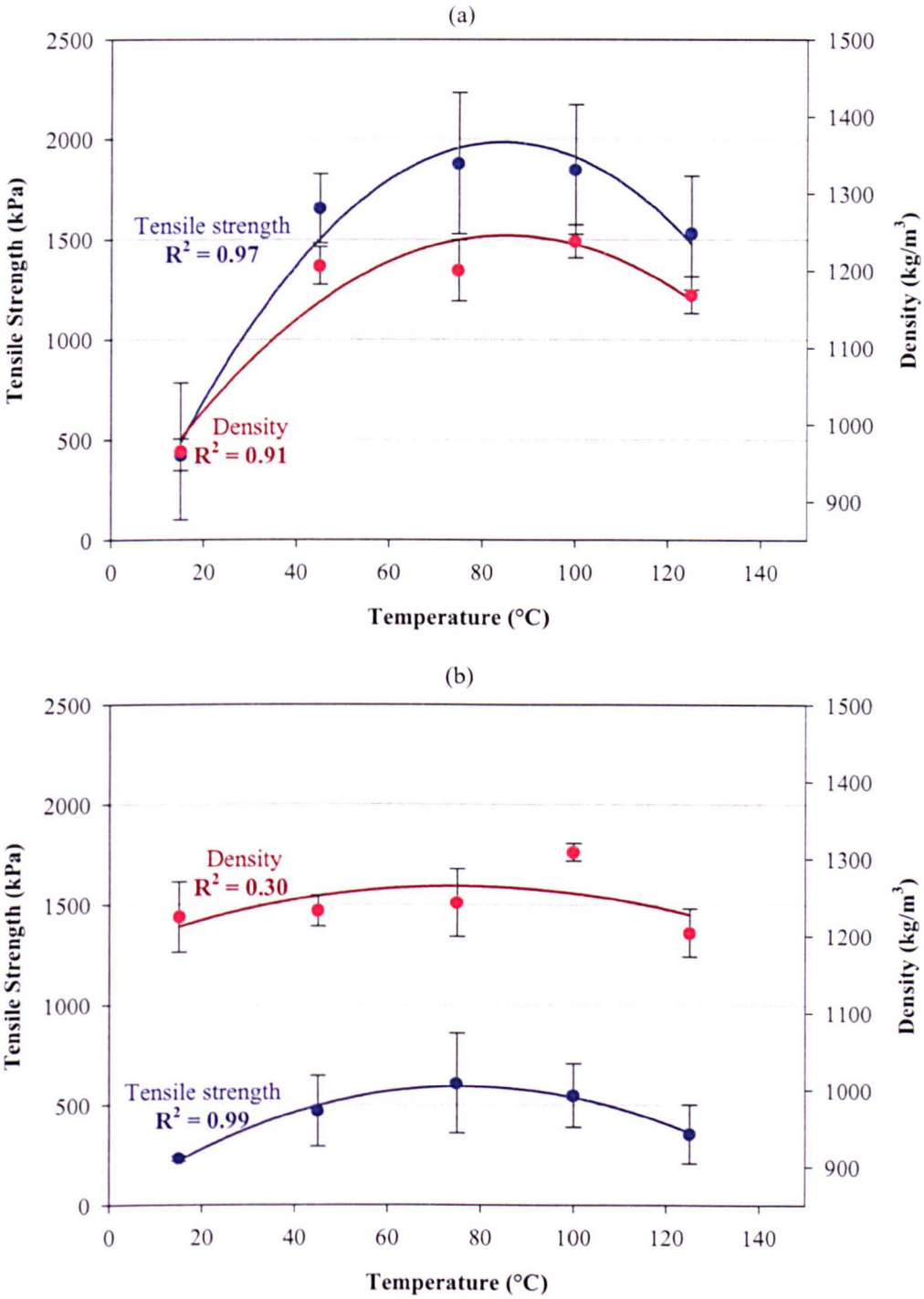


Figure 7.18: Plots of the effect of pelletisation temperature on the tensile strength and density of (a) SMC pellets and (b) SMC-coal tailing pellets. 95% Confidence Limits are shown as error bars.

The maximum heights of the pellet piles were computed (Table 7.5). As suggested by the tensile strengths and densities, pellets made at elevated temperatures (45 and 75 °C) should be able to withstand significantly higher pellet piles without being damaged. SMC pellets performed consistently better than the mixture of these wastes, particularly at 75 °C, where pellets are thought to be able to withstand

heights in excess of 300 m. Piles of this magnitude would obviously not be practicable, but indicate that storing these pellets in piles would not be detrimental to their quality. This temperature also considerably increased the pile height for SMC-coal tailing pellets, though not to the same extent. As seen from Table 7.5, high tensile strengths are required to stack the pellets, although depending on the type of storage, durability may also be a factor, particularly during delivery to the storage facility. There are a range of storage options for such pellets; these include: (i) simple open/covered stores, which are cheap and fuel delivery is straightforward; (ii) underground bunkers, which make fuel delivery easy but are only economic for large-scale systems; (iii) hook-lift bins, which are practical if there is restricted storage space but can cause difficulties with delivery; and (iv) hoppers, which complicate delivery options and require specific machinery, but are often used when there is limited space available (Hodsman and Smallwood, 2004). The use of any of these would restrict the maximum pile height and thus the optimum would be lower than both the maximum heights calculated here and that limited by the storage facility.

VARIABLES AND PARAMETERS	PELLETISATION TEMPERATURE (°C)									
	RT	45	75	100	125	RT	45	75	100	125
SMC:Coal Tailings	100:0	100:0	100:0	100:0	100:0	50:50	50:50	50:50	50:50	50:50
Pellet Length (mm)	38.1	34.9	37.7	33.8	38.8	33.8	35.9	33.8	33.5	38.2
Density (kg/m^3)	965	1195	1200	1238	1168	1224	1232	1243	1308	1204
Compressive Strength (N)	675	2440	2960	2630	2490	332	710	930	770	575
Weight (kg)	69.0	249.0	302.0	268.4	254.1	33.9	72.5	94.9	78.6	58.7
Number of Pellets	3322	10581	11835	11376	9948	1449	2905	4000	3174	2261
Height of Pellet Pile (m)	**89.0**	**283.6**	**317.2**	**304.9**	**266.6**	**38.9**	**77.9**	**107.2**	**85.1**	**60.6**

Table 7.5: Results for the maximum heights of pellet piles at elevated temperatures, comparing SMC pellets and SMC-coal tailing pellets.

Durability experiments compared pellets made at room temperature to those made at the optimum and elevated temperatures, 75 °C and 125 °C respectively, for both SMC and SMC-coal tailing mixtures (Table 7.6). Pellets made at 75 °C were more durable, losing significantly less mass over time, for both compositions compared to those made at room temperature. As above, further heating does not produce additional improvements in pellet quality, thus extreme heating (~125 °C) of the materials is disadvantageous, both in terms of pellet quality and energy expenditure. SMC pellets were more durable than the mixture, which was also reflected in the results of the tests above.

TEMP (°C)	DURABILITY: % MASS REMAINING	
	SMC	SMC-Coal Tailings
RT	78.57	32.54
75	93.96	54.85
125	76.25	22.40

Table 7.6: Durability of SMC and SMC-coal tailing pellets made at elevated temperatures.

These studies demonstrated that pelletisation at elevated temperatures was beneficial to pellet quality in terms of density, tensile strength, pellet pile-up and durability for these materials. At these temperatures, it was thought that any lignin present in the SMC softened and acted as a binder – there was a clear

thermal effect on these materials. Increasing the temperature beyond 75 °C, however did not further improve pellet quality and possibly led to lignin degradation. As lower temperatures are cheaper to maintain, slight temperature increases are convenient in terms of pelletisation costs and pellet quality.

7.9.2 Effect of Pelletisation at Elevated Temperatures with a Binder

Based on the optimum temperature (75 °C) and the optimum amount of binder (1 wt%), tests were carried out to investigate the combination of these, to see if further improvements could be made to pellet quality. The use of the binders coupled with elevated temperatures produced improvements in pellet quality compared to the use of these binders alone, although pelletisation using only elevated temperatures was generally superior (Table 7.7). Durability and density, however, were seen to improve for both binders at 75 °C. ANOVA tests showed that the improvements seen with the use of temperature and the binders (compared to the binders used at room temperature) was only significant for density, not tensile strength.

BINDER	AMOUNT OF BINDER (%)	TEMP (°C)	DENSITY (kg/m^3)	TS (kPa)	MAX HEIGHT OF PILE (m)	DURABILITY: % MASS REMAINING
Caustic Soda	0.0	RT	1224.1	233	38.85	32.79
	1.0	RT	1171.6	360	62.92	40.38
	0.0	75	1242.7	609	107.21	54.85
	1.0	75	1285.7	400	63.64	62.17
Starch	0.0	RT	1224.1	233	38.85	32.79
	1.0	RT	1147.5	411	73.05	31.94
	0.0	75	1242.7	609	107.21	54.85
	1.0	75	1296.1	463	72.88	67.57

Table 7.7: Results for density, tensile strength, pellet pile-up and durability of SMC-coal tailing pellets made with a binder at elevated temperatures.

7.9.3 Effect of Steam Pelletisation

Pellets were manufactured using a 50:50 wt% ratio of SMC:coal tailings, where the materials had been conditioned for varying lengths of time, from 2.5-10 mins. The data concerning the differences in densities, tensile strengths and pellet pile-up results were examined and compared to pellets manufactured without steam conditioning. Any improvements could then be contrasted to those seen with the use of elevated temperatures or the addition of a binder. As shown on Figure 7.19, the tensile strength increased with the duration of steam conditioning, up to 5 mins, after which the tensile strength decreased. The pellets for 3.25 mins and 6.25 mins of conditioning were manufactured when the laboratory was significantly cooler than for the other pellets, leading to the moisture condensing on the pellets after conditioning, thus increasing their moisture content and reducing their tensile strength. It has been previously investigated that moisture is a significant pelletisation variable and if the optimum is not used, in this case 10-11 %, there can be detrimental impacts on pellet quality. Density appeared to follow the opposite trend, primarily due to expansion and cracking of the pellets during drying after manufacture. As with pelletisation at elevated temperatures, steam conditioning appeared to soften the lignin and enhance the agglomeration of the particles up to a certain point.

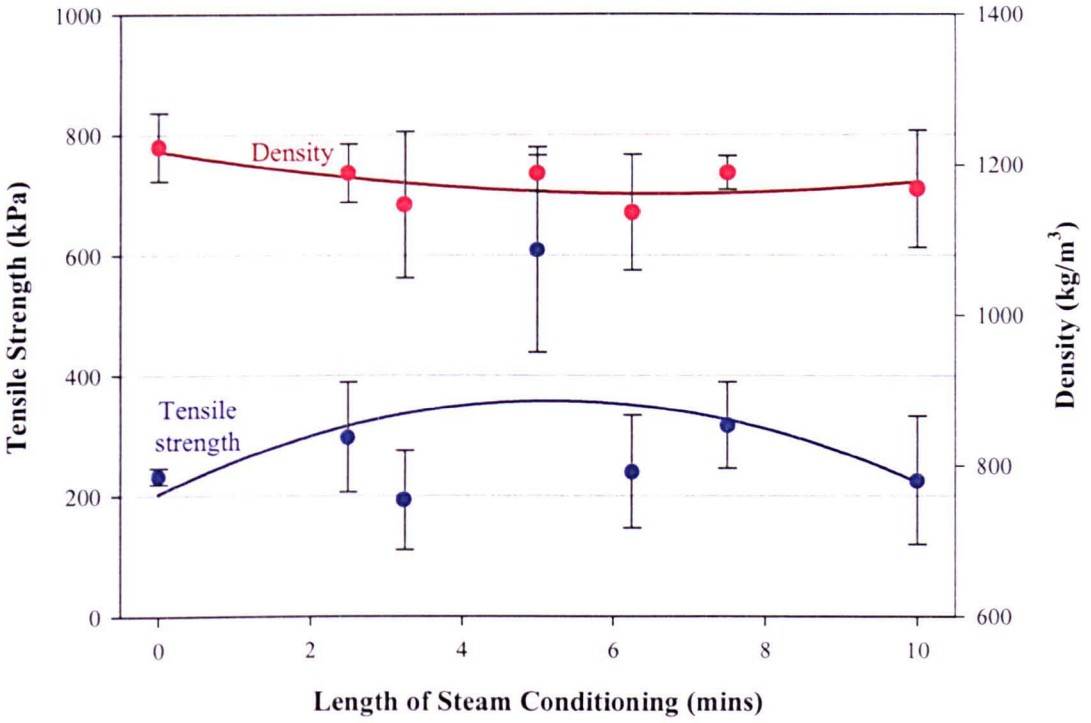


Figure 7.19: The impacts of steam conditioning on the density and tensile strength of 50:50 wt% SMC-coal tailing pellets. 95 % Confidence Limits are shown as error bars.

5 mins of steam conditioning produced pellets with a tensile strength of ~600 kPa, similar to the results for pelletisation at 75 °C. There appeared to be greater variation in these results, however, and ANOVA tests found that the only significant results were for tensile strength when comparing 5 mins of steam conditioning to no conditioning, where the *P-value* was 0.003. There were no statistical differences for density for any of the comparisons made. The maximum pellet pile heights for various conditions were computed (Table 7.8). As indicated by the increases in tensile strength, the pile height of SMC-coal tailing pellets could be increased using steam additions. The optimum amount of conditioning (5 mins) could increase the height of the pile to over 100 m, again similar to heating the materials to 75 °C.

VARIABLES AND PARAMETERS	LENGTH OF STEAM CONDITIONING (min)				
	none	2.5	5	7.5	10
Pellet Length (mm)	34	39	36	37	36
Density (kg/m^3)	1224	1189	1189	1190	1168
Compressive Strength (N)	332	486	924	501	342
Weight (kg)	33.9	49.6	94.3	51.1	34.9
Number of Pellets	1450	1905	3905	2048	1455
Height of Pellet Pile (m)	**38.85**	**51.05**	**104.67**	**54.87**	**38.98**

Table 7.8: The heights of SMC-coal tailing pellet piles for various durations of steam conditioning.

7.10 DISCUSSION AND CONCLUSIONS

The results from the numerous case studies outlined above have meant that the optimal values for a number of variables were determined when manufacturing these wastes into fuel pellets. The most important pelletisation parameters described in the theoretical chapter were also found to be those that primarily impacted pellet quality here. As considered above, these included an initial moisture content of

10-11 %, a pelletisation pressure of 2500-6000 psi (17.2-41 MPa), which Rieschel (1963) classifies as low pressure, and complete air drying after manufacture, for a 50:50 wt% SMC-coal tailing ratio. This ratio produces pellets that deform, not break, due to the flexibility of the intertwined fibres within a matrix of small particles. Holding time was deemed to have a less influential impact than in the tests of Jones (1969) and Li and Liu (2000). Pelletisation of these materials under unsuitable conditions produced a product weak, that could only withstand low pellet pile heights and were not durable. Pellets of the optimum SMC:coal tailing ratio performed well in both the pellet pile-up and durability tests. They can withstand a height of up to 12.1 m and on average lost 30 % of their mass in the durability tests.

Whilst utilising the optimum conditions significantly enhanced fuel quality, further studies to improve pellet quality could reduce friability. Small amounts (1 wt%) of both binders increased tensile strength and the maximum pellet pile height, where starch had more pronounced effects, doubling the tensile strength to 411 kPa. Pellets made with NaOH, however, were more durable, whereas starch slightly decreased durability compared to those without a binder. Furthermore, it was anticipated that starch would impact the thermal treatment of these fuels less than NaOH, which was subsequently tested. Thus, starch appears to be more favourable for this application. Elevated temperatures and steam conditioning improved all pellet quality assessment criteria; the former enhanced overall fuel quality more significantly than the use of either binder, increasing the tensile strength to over 600 kPa, although additional temperature increases (up to 125 °C) did not result in further improvements. Similar results were noted using 5 mins of steam conditioning, although as greater temperatures are required to generate superheated steam, the use of elevated temperatures is likely to be more economic. Pellet quality improvements were not as large with the additions of the binders compared to the use of elevated temperatures, however, as purchasing them is likely to incur a minimal cost and their application is simple, binders are likely to be favoured commercially. Whether a binder or elevated temperatures are used during pelletisation is strongly dependent on the comparative costs of these options, relative to improvements in product quality.

High tensile strengths will be needed to store pellets without damaging them, especially as they will be stacked in large volumes. It is therefore vital that pile heights do not exceed the maxima outlined above, so pellet quality is not compromised. Pellet pile height would also be restricted by the storage facility. Storage for lengthy periods of time is not recommended, as it can be detrimental to pellet quality, particularly durability (Lehtikangas, 2000). For transportation, handling and feeding, for example using a screw feeder, durability (tested by resistance to abrasion and mechanical impacts) plays a more important role; extensive handling and feeding phases can lead to dust formation, which may cause mechanical problems, as well as lead to a reduction in the amount of fuel that is fed into the combustor. It is crucial that the pelletisation conditions produce adequate pellet tensile strengths and durability, to minimise difficulties with all aspects of storing and using these pellets; for these materials, elevated temperatures (45-75 °C) improved fuel quality the most. Despite the superior influences of pelletisation at 75 °C, the process economics, as explored subsequently, are likely to be the driving factor in the decision making.

8

INITIAL COMPARISON OF THERMAL TREATMENT TECHNOLOGIES

8.1 INTRODUCTION

A range of thermal treatment tests were performed on the materials, which is the third phase of the experimental programme. Three thermal treatments – combustion, gasification and pyrolysis, outlined in Section 3.2 – were performed in a series of initial tests, involving the comparison of SMC and the SMC-coal tailing pellet combustion in two vessels, which allowed the assessment of combustion characteristics and behaviour. These were contrasted to the gasification and pyrolysis of the raw, unpelletised SMC, which was air-dried to aid its treatment, resulting in a material with a decidedly lower bulk density. From these preliminary tests, recommendations were made on the future direction of the project. Here, the experimental design and specific variables for these tests are described, along with the results for each of the thermal treatment processes.

8.2 PELLETISATION OF MATERIALS ON A MASS SCALE

As several kilograms of pellets were needed to perform such tests, a mechanised pelletisation rig was designed and built to make two types of pellets for this stage of the investigation. The first were small pellets for the laboratory-scale fluidised-bed (Type 1) and the second were larger pellets for the packed-bed reactor (Type 2). These were made using a pelletiser at the Buxton laboratories of the University of

Sheffield. Schematics and a photograph of this pelletiser and its set-up are shown in Figures 8.1 and 8.2. The rig was optimised so that good quality pellets could be formed; these alterations involved the additions of teeth to the rollers, but also the removal of the hopper, seen in Figure 8.2, as placing the material on the base plate was better, shown in Figure 8.1.

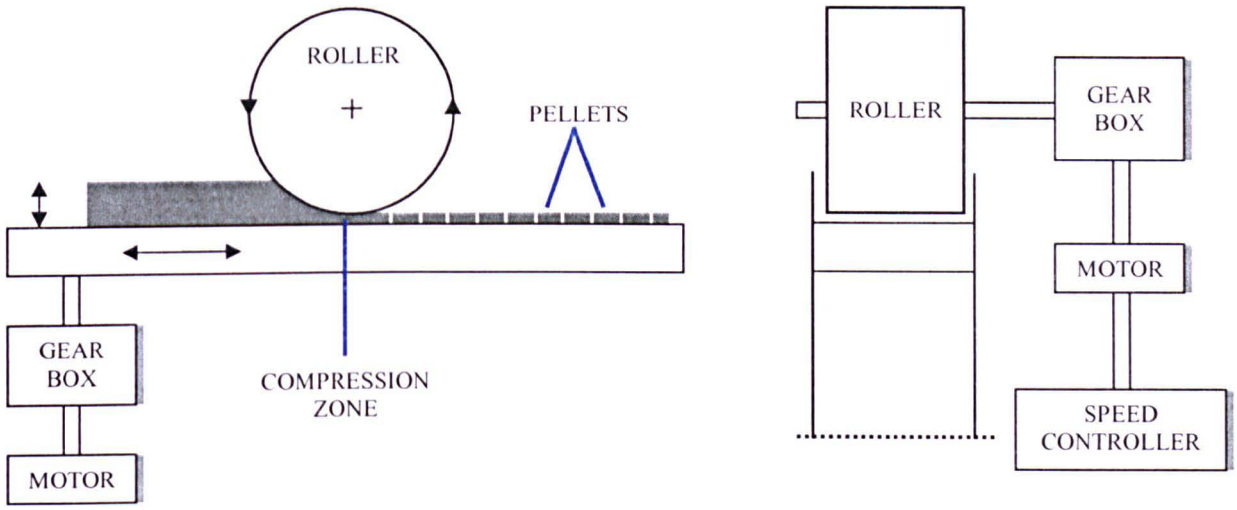


Figure 8.1: Annotated side and front view schematics of the mechanised pelletisation rig.

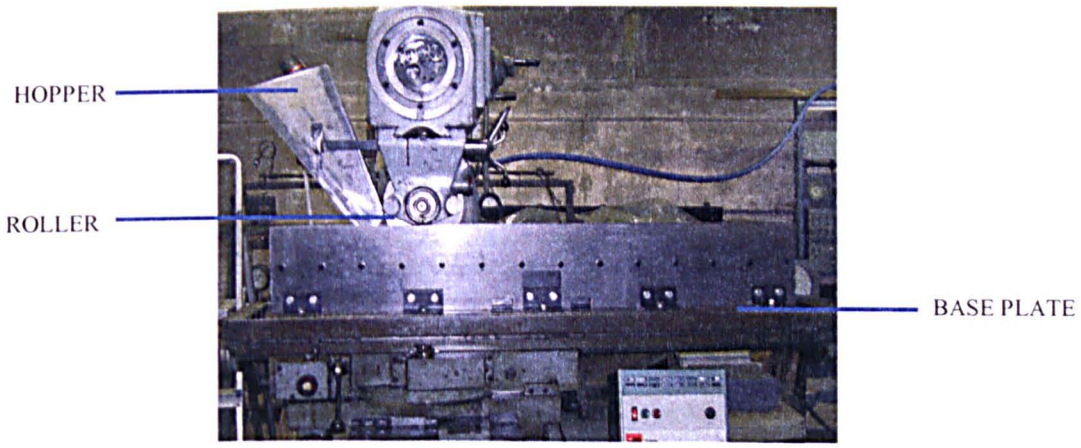
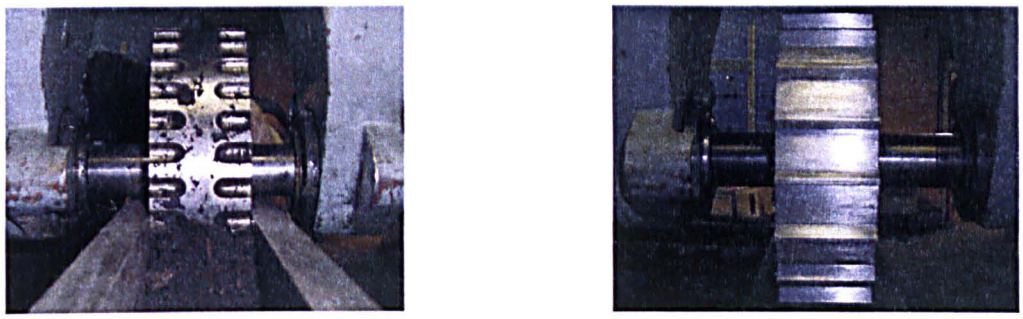


Figure 8.2: Side view photograph of the mechanised pelletisation rig.

The SMC and coal tailings were dried to 10-11 % moisture and thoroughly mixed in a 50:50 wt% ratio. The moisture of the initial materials used for pelletisation was significantly higher than that of the dried pellets, as the particles' plasticity needed to be increased to aid pellet formation and encourage bonding, considered in Chapters 5 and 7. During pelletisation, the material was drawn into the compression zone identified on Figure 8.1, which compacted the material between the plate and the roller. The teeth on the roller both aided the feeding of the material into the compression zone and formed the shape of the pellets. The pellets were then fully air-dried, to about 2-4 % moisture. Other modes of pelletisation, such as extrusion, may require different conditions and material properties for pelletisation to be optimal. The different rollers/roller-die combinations used to produce various pellets suitable for these applications are shown in Figure 8.3, along with the pellets formed using these respective rollers in Figure 8.4. A comparison of their properties and manufacturing conditions are given in Table 8.1.



(a) (b)

Figure 8.3: The rollers and die used to form (a) small pellets for the preliminary laboratory-scale fluidised-bed tests – Type 1, and (b) the larger pellets for the packed-bed tests – Type 2.

Type 1 Type 2

Figure 8.4: Type 1 and 2 pellets (actual size) for the fluidised- and packed-beds.

PROPERTY		TYPE 1	TYPE 2
Size	*a*-axis (mm)	20	58
	b-axis (mm)	12	28
	c-axis (mm)	7	12
Density	pellet (kg/m^3)	687.4	800.0
	bulk (kg/m^3)	449.9	331.9
Pelletisation Conditions	roller speed (rpm)	3	3
	base plate speed (mm/min)	615	615

Table 8.1: Comparison of the pellets made with the different rollers on the mechanical pelletiser.

8.3 DESCRIPTION, ANALYTICAL SETUP AND OPERATIONAL PROCEDURES OF THE REACTORS

A fluidised-bed combustor, a fixed-/packed-bed reactor and a pyrolyser were used to carry out the various preliminary thermal treatment tests on these waste materials. This section contains a description of the components of each rig, the experimental set-ups used and their start-up and shut-down procedures.

8.3.1 Laboratory-Scale Fluidised-Bed

The atmospheric, bubbling, laboratory-scale fluidised-bed combustor, of which a schematic and a photograph are shown in Figures 8.5 and 8.6 respectively, was initially designed to generate 10 kW of

energy. It consisted of a combustion chamber that was fed with primary air from a nozzle distributor in the base, which acted as both the fluidising and combustion air; the fuel was fed from the hopper into the combustion zone using a pneumatic screw feeder. The sand bed, which was heated using the pilot burner, rested on a distributor plate. The gas concentrations and temperatures were monitored throughout the reactor and the flyash was collected by the cyclone. These key components are described below.

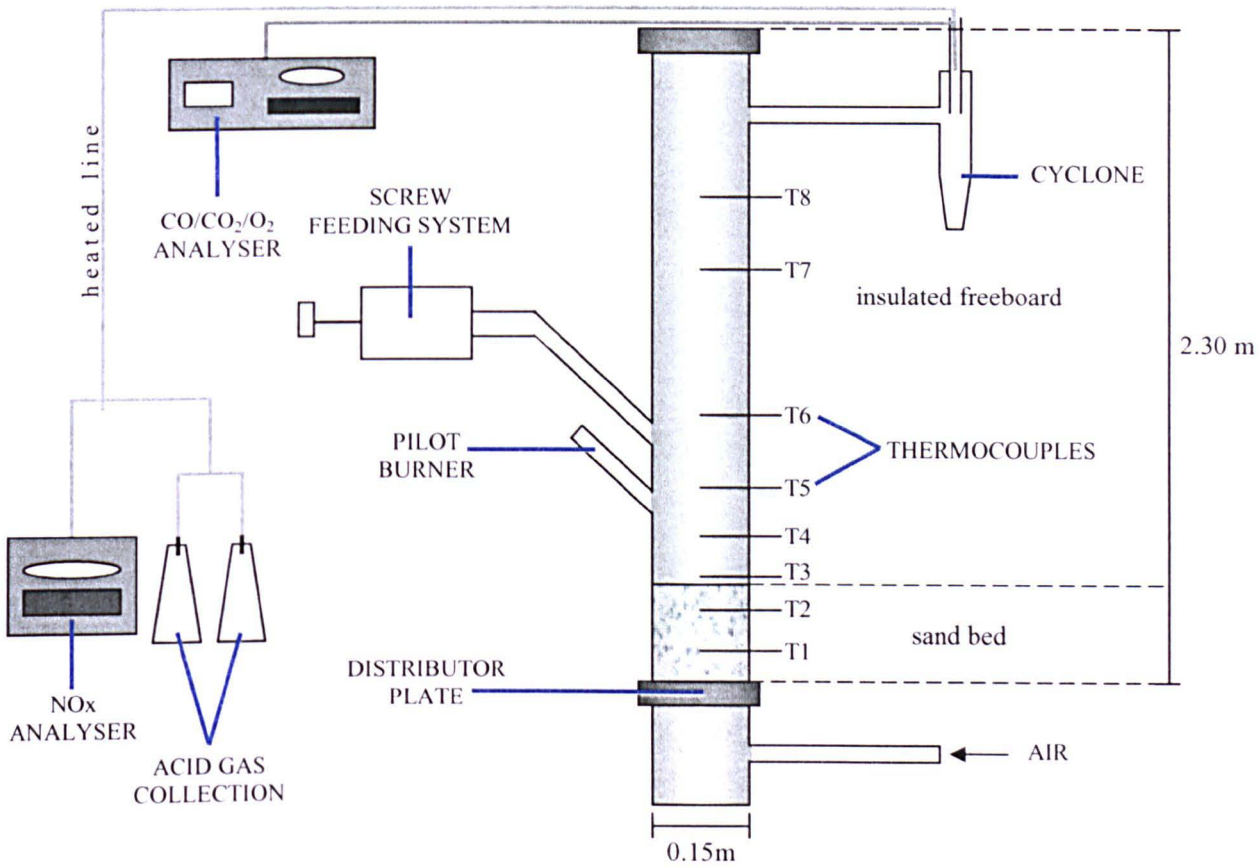


Figure 8.5: Schematic of the set-up for the laboratory-scale fluidised-bed used for the combustion of the fuel for the preliminary tests.

8.3.1.1 Combustion Chamber

The combustion chamber was made of 1 cm-thick 306 stainless steel, which was 2.3 m high with an internal diameter of 0.15 m. The medium sphericity (sub-rounded to sub-angular) sand that formed the fluidised-bed had an average diameter of 850 μm. The depth of this sand bed within the reactor could be up to 0.3 m, and thus the freeboard height above this was at least 2 m; the freeboard section of the chamber was insulated with a Kaowool blanket, as shown in Figure 8.6.

8.3.1.2 Distributor Plate and Air Distribution

Primary air, used for fluidisation and combustion, was introduced to the bed and combustion chamber from the compressor through a nozzle in the 10 mm-thick stainless steel distributor plate, located 200 mm from the base of the reactor. This plate had nineteen 6 cm-high capped standpipes, each with twenty-seven 1.5 mm diameter holes to evenly distribute the air through the bed. A stationary layer of sand was able to insulate the plate from the hot bed above, and thus a separate cooling system was not required.

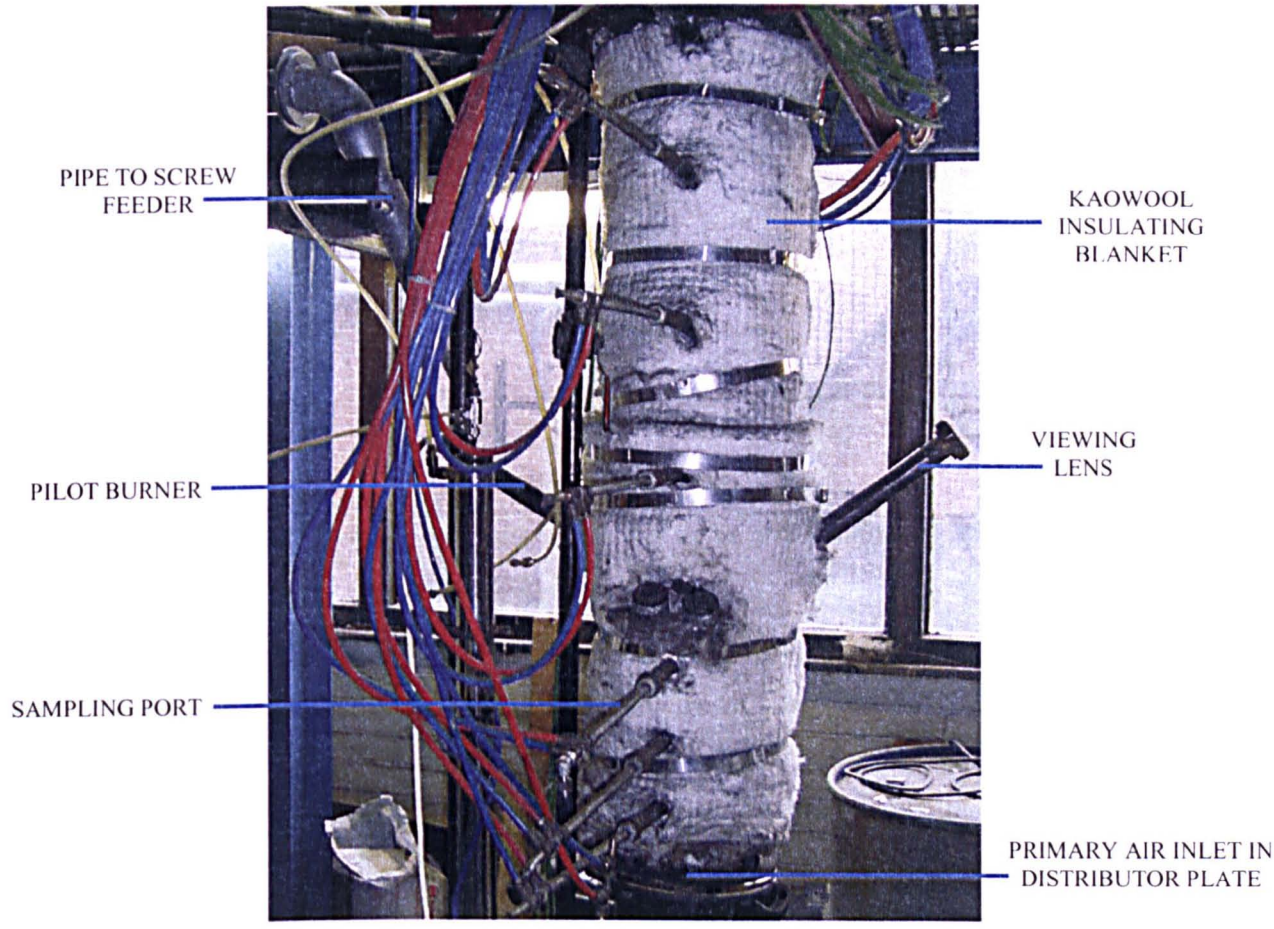


Figure 8.6: Photograph of the laboratory-scale fluidised-bed combustor.

8.3.1.3 Pilot Burner and Viewing Lens

The pilot burner was located at an angle port, as shown above, to aid the initial heating of the bed. This was tested and inserted at the start-up stage to ignite the propane used to pre-heat the bed, and was then extinguished and withdrawn from the reactor for the combustion tests. A viewing window with a quartz glass lens was located opposite so the pilot light flame could be observed. Appropriate fluidisation could also be assessed this way.

8.3.1.4 Pneumatic Screw Feeding System

The fuel material, either the SMC-coal tailing pellets or the unpelletised, dried SMC, was placed into the sealed hopper of the K-tron Soder pneumatic screw feeding system and was fed into the combustor at the sand bed surface through an inclined pipe, 45 ° to the combustion chamber. This feeding pipe, 0.7 m above the distributor plate, was cooled using a water jacket to ensure combustion did not occur before the fuel reached the chamber. The hopper was also operated under slightly positive pressure to ensure that combustion gases did not enter into the feeding system; due to this, some secondary combustion air was introduced with the fuel. The fuel feedrate was calibrated before the combustion experiments began, by utilising a variety of screw speeds to construct a graph of the fuel feedrate against the screw rpm (Figure 8.7). Spiral and auger screws were used to feed the pellets and SMC respectively, where the feedrate was controlled by altering the rotation speed of the screw.

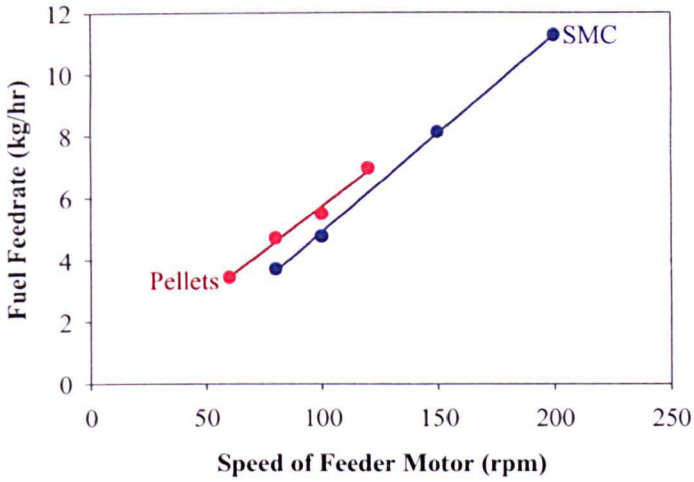


Figure 8.7: Correlations for motor speed and fuel feedrate for the spiral (SMC-coal tailing pellets) and auger (SMC) screws.

8.3.1.5 Experimental Setup and Operational Procedure

The fuel was prepared, either by drying the SMC or by drying, mixing, pelletising and further drying for the SMC-coal tailing pellets. The fuel was then placed into the calibrated hopper. The gas analysers used to monitor the exhaust gases and the thermocouples used to monitor the temperature were checked and calibrated, where necessary. These were monitored and logged throughout the duration of the experiment; the rpm of the screw feeder also needed to be noted so the feedrate could be established. Next, the water lines and the extractor fan were switched on, then the pilot burner, used for ignition, was removed for testing, before being replaced at the correct bed depth. The fluidising air was subsequently turned on to a high flowrate (e.g. 420 l/min) for 5 mins to unblock the bed and was gradually turned off. The gas-fired pilot burner was lit and the propane valve opened to be ignited and heat the bed; the propane was increased until the minimum fluidising air level was reached. Monitoring the thermocouples was necessary to ensure the bed heated evenly; when the temperature was even and stable (approximately 800 °C), the air and propane flowrates were reduced. If the pilot light was extinguished, the propane was turned off, and the system purged with air before the burner was relit. Once the chamber was stable, the fuel was fed in, increasing the feedrate as the propane flowrate decreased.

The normal shut down procedure for this rig was simple; the fuel feeding was stopped by turning off the screw feeder system. The flowrates of the cooling water and the fluidising air were then increased and once the bed was sufficiently cooled, these could also be turned off. Lastly, the data logging devices and safety valves were switched off.

8.3.2 Packed-Bed Reactor

A packed-bed reactor (Figures 8.8 and 8.9) was also used to combust the pellets and dried SMC, to compare the results to those from the fluidised-bed; this rig was also used for the gasification of the unpelletised SMC. It consisted of a reaction chamber with a grate at the bottom, on which the fuel was placed; the fuel was ignited with the burner as the chamber was fed with combustion air.

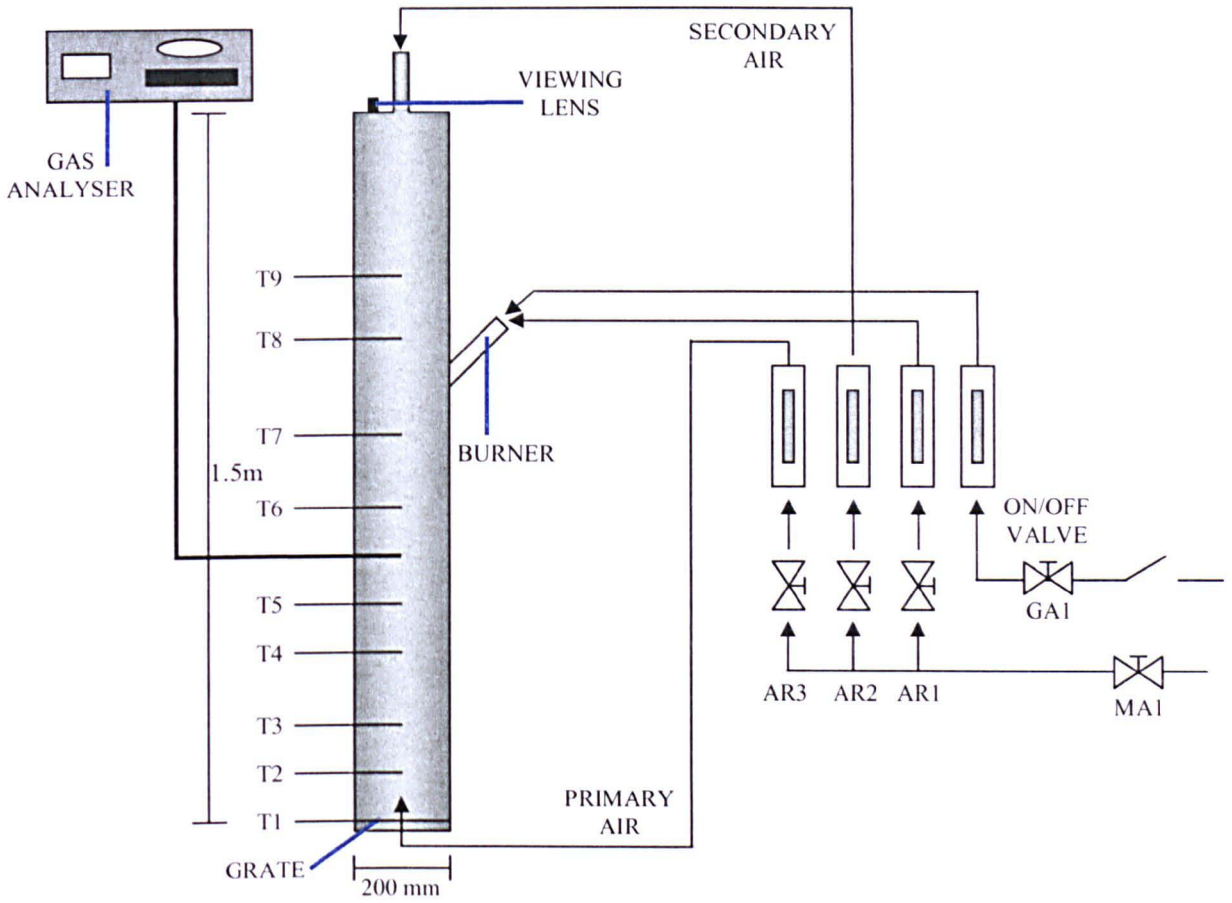


Figure 8.8: A schematic of the packed-bed reactor used for thermal treatment.

8.3.2.1 Reaction Chamber and Weighing Beam

The vertical reactor consisted of a 1.5 m high stainless steel chamber with an internal diameter of 0.2 m; the primary and secondary air feeds were at the bottom and top respectively. The chamber was lined with a heat-resistant refractory material so the temperatures could reach 1300 °C without damaging the reactor. The combustor was suspended from a weighing beam to monitor weight-loss during the thermal treatment of the fuel. The fuel pellets or non-pelletised SMC were placed into the reaction chamber before the burner was ignited.

8.3.2.2 Perforated Grate and Air Distribution

Within the chamber, a perforated grate was located at the bottom, upon which the fuel rested. The grate, as seen on Figure 8.9, had a series of small orifices to allow the primary combustion air to flow through the chamber. Once the reaction was completed and the reactor had cooled, the ash, which remained on the grate, was removed for analysis.

8.3.2.3 Starter Burner

A gas burner, located at one side, 0.75 m above the grate, was fed with air and gas to ignite the fuel and also for initially heating the chamber. A viewing lens was located at the top of the reactor, to ensure that the burner had ignited and so the combustion of the fuel could be observed.

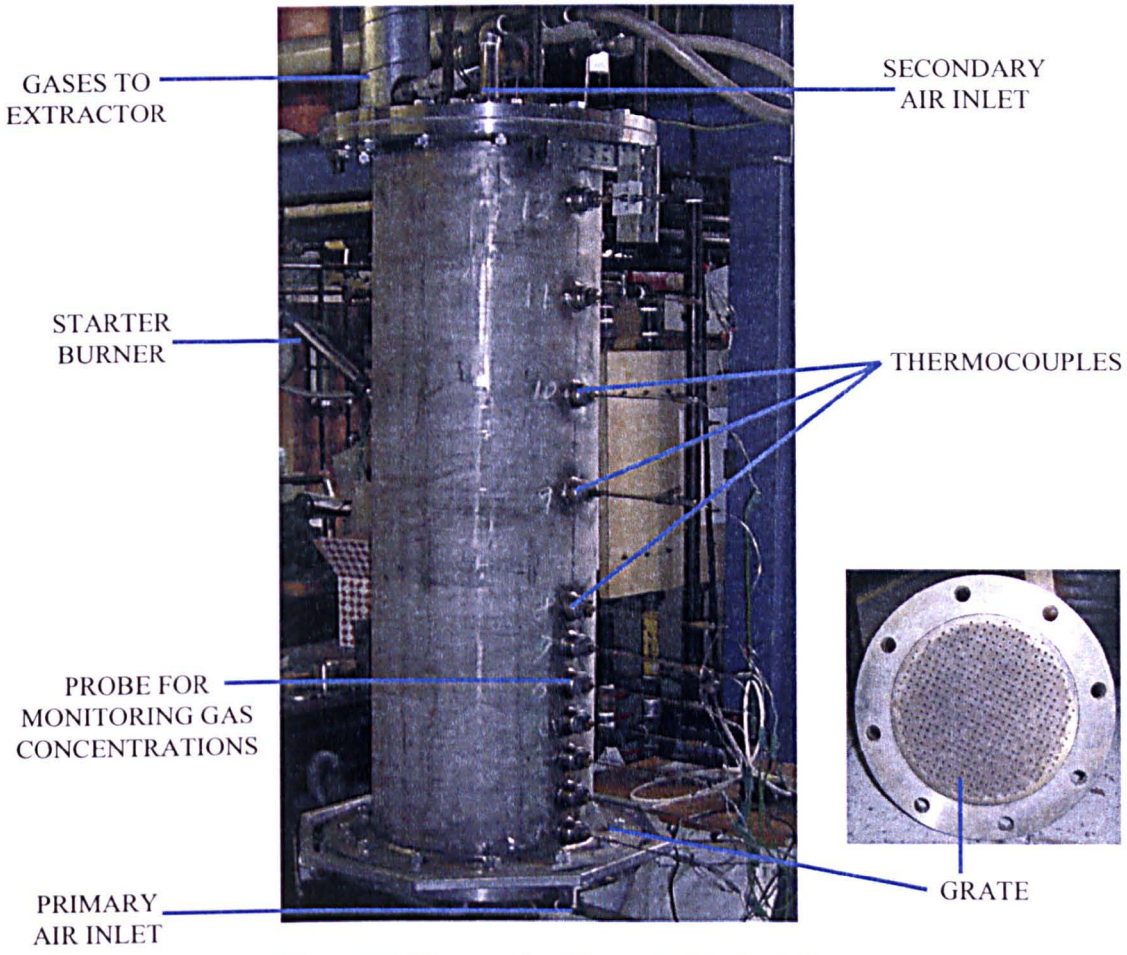


Figure 8.9: Photographs of the packed-bed and the grate.

8.3.2.4 Experimental Setup and Operational Procedure

The normal start-up procedure was as follows. The analysers and pumps needed to warm up, so were switched on for approximately one hour before the packed-bed combustor was used; the gas analyser also needed to be calibrated. Water was then allowed to flow to the cooling tower and the scale indicator was set to zero. Next, the pre-weighed fuel was fed into the combustor and the lid fastened; at this point, the sample weight was checked. It was also important to ensure that all ports were air tight. The extraction fan was switched on and the rotameter valves shut; the main compressed air valve (MA1), the primary air (AR3), and the air to the burner (AR1) were turned on; the secondary air (AR2) could be used if required. The system was now ready for ignition; power (SW1) and gas (GA2) were required so the burner ignitor could be fired, where GA1, the on/off valve, needed to be open. The flame should be checked once lit. Logging of the weight loss, temperature and gas concentrations could begin, and the readings of the temperature in the freeboard needed to be checked to ensure the thermocouples were working.

Normal shut-down of the system began with the switching off of the gas (GA1 and GA2) and the air (AR1). The Variac controller was gradually turned to zero, and the power switched off (SW2). Next, the valves for primary (AR3), secondary (AR2) and main air (MA1) were turned off and the temperature, weight and gas loggers were stopped. The analysers were disconnected and left to flush out before being turned off. Lastly, the extraction fan and the water (TA1) to the cooling tower were switched off.

8.3.3 Pyrolyser

As with gasification to evaluate the potential of SMC, pyrolysis – a thermal degradation process in the absence of air – was also performed. The pyrolyser, shown in Figures 8.10 and 8.11, was used to perform this test on dried SMC. It consisted of a primary fixed-bed reactor, where nitrogen was fed through the bottom to ensure the volatiles were forced out through the top of the chamber, to the subsequent condensing and analysing equipment; these components are described below.

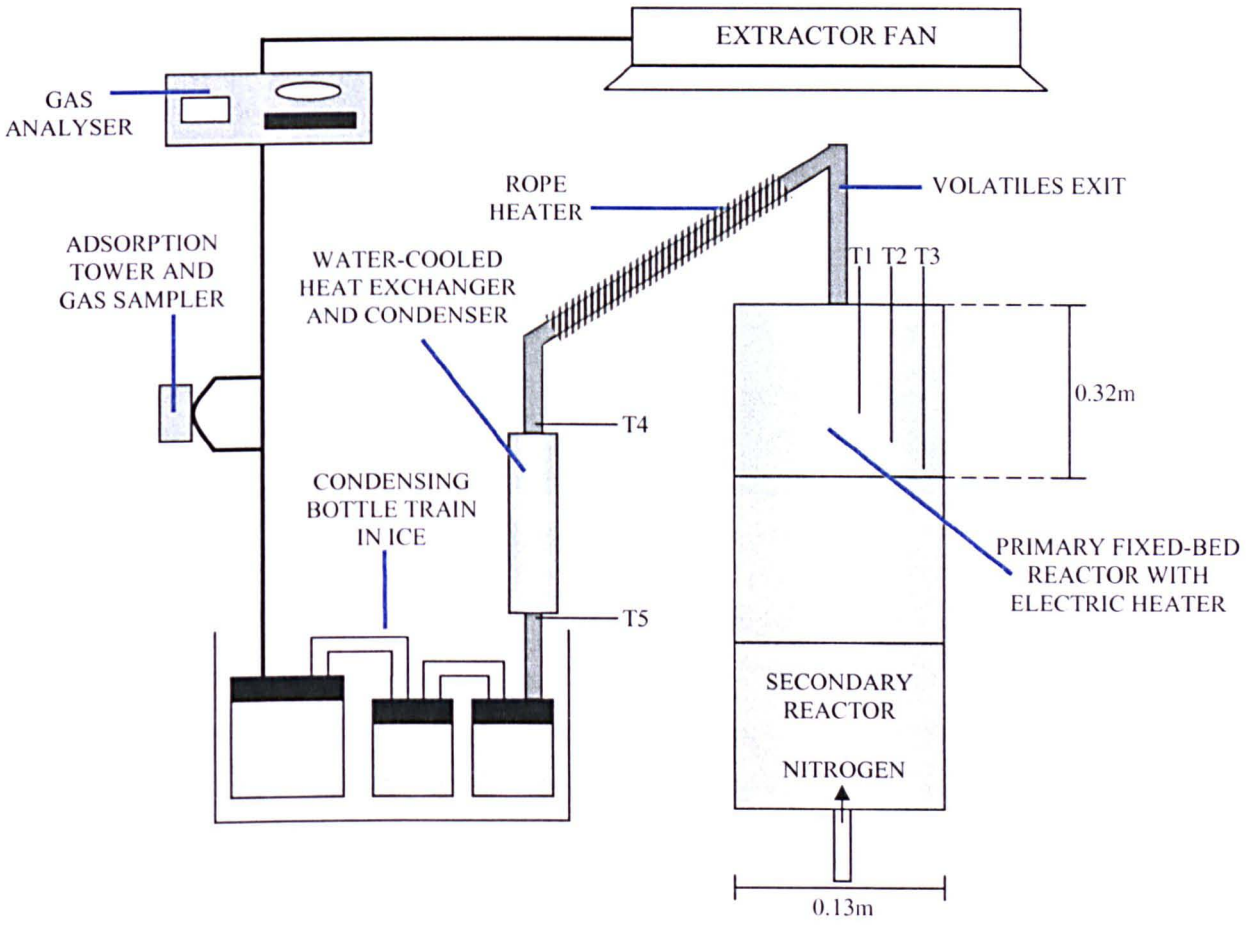


Figure 8.10: A schematic of the pyrolyser used for the pyrolysis of the SMC.

8.3.3.1 Heated Primary Reactor

The material was placed in the 130 x 320 mm stainless steel primary fixed-bed reactor at the top of the pyrolysis chamber; this was electrically heated and thoroughly insulated. The secondary reactor was not used in this instance. During the reaction, char was formed, which remained inside the reactor chamber. This was fed with nitrogen at the base to prevent oxidation and to force the volatiles that were released out at the top, into the subsequent heat exchanger and analysing equipment.

8.3.3.2 Volatiles Exit, Condenser and Condensing Train

The volatiles released passed through a pipe, heated by rope heaters to ensure the gases did not condense in the pipe work. They were then partially condensed by passing them through a counter-flow heat exchanger; the gases were cooled and some condensed into pyrolytic liquids, collected using the three

cooled bottles in the train, weighed prior to and after the test. The remaining gases were fed through a condensing tower; samples were taken at specific temperatures to assess the changing syngas (gaseous fuel product) composition. These then went to the gas analyser for analysis and the exhaust was fed to the extractor fan. In addition to these gases, the pyrolytic liquid and char produced were also analysed.

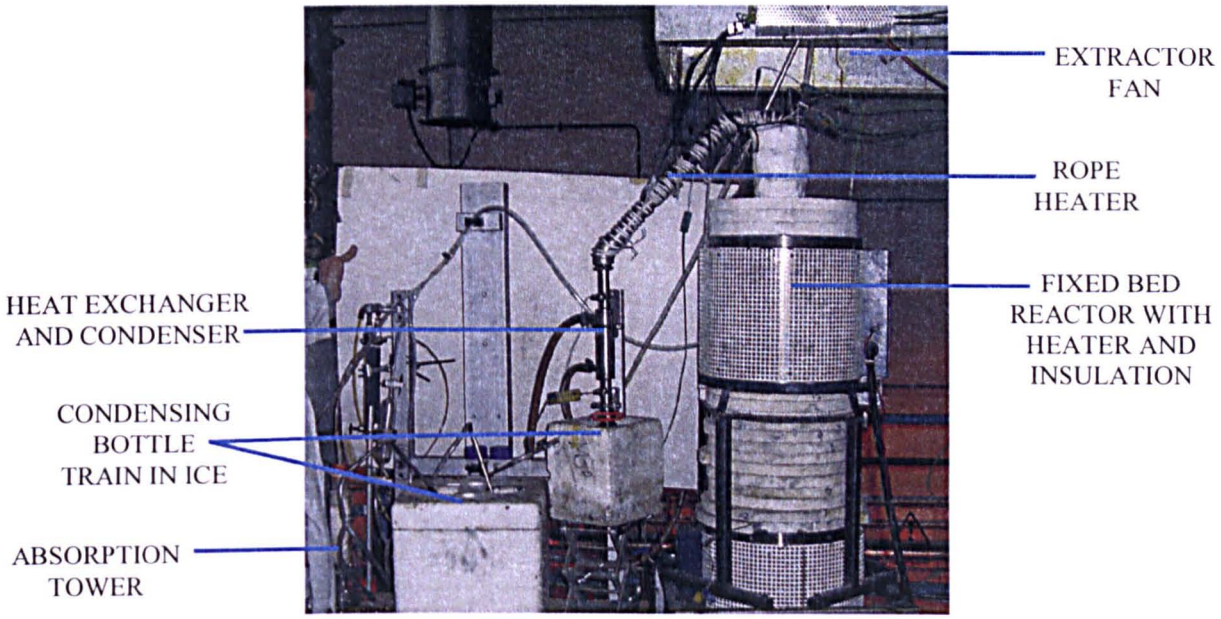


Figure 8.11: Photograph of the pyrolyser.

8.3.3.3 Experimental Setup and Operational Procedure

The normal start-up procedure for the pyrolyser was as follows. First of all, the material, in this case air-dried SMC, was placed into the reaction chamber. The nitrogen was then switched on at 2 l/min and run through the reactor to ensure any oxygen that may alter reactions was removed and that the volatile material released from the SMC flowed out at the top and through the heat exchanger. The gas analyser also required calibration at this point. It was necessary to pre-heat the reactor, as the temperatures can vary significantly; the reactor was heated and the running time was not begun until a steady and correct pyrolysing temperature was achieved. This temperature could be modified using the temperature controller; at this point, the extractor fan was also started. Once the temperature was stable, the data loggers, thermocouples and heat exchangers were switched on to record data.

Once the pyrolysis reactions had been completed, the shutdown procedure could ensue. Initially, the data loggers were stopped. Subsequently, the temperature controller was turned off and the heat exchangers stopped. Lastly, the extractor fan was shut down.

8.4 EXPERIMENTAL DESIGN AND OPERATING CONDITIONS

8.4.1 Combustion in the Laboratory-Scale Fluidised-Bed

Two preliminary combustion tests were completed in the laboratory-scale fluidised-bed. These compared the differences in the combustion behaviour of Type 1 SMC-coal tailing pellets to that of the unpelletised,

dried SMC. This would assess whether pre-processing, specifically combining the SMC with coal tailings, followed by pelletisation, was necessary. Whilst the bed depth was constant for these tests, a range of primary air flowrates and fuel feedrates were examined for both cases, as seen in Table 8.2. This bed depth resulted in a pressure drop of 4.44 kPa, calculated using Equation 4.2.

CASE	PRIMARY AIR (kg/m^{2}hr)	FUEL FEEDRATE (kg/hr)	DEPTH OF SAND BED (m)
Pellets	240 – 610	1.7 – 5.7	0.3
SMC	190 – 770	1.7 – 3.9	0.3

Table 8.2: Operating conditions used in the two preliminary experiments in the fluidised-bed.

8.4.2 Combustion in the Packed-Bed Reactor

Two similar combustion experiments were conducted in the packed-bed, to also compare the combustion behaviour of the SMC-coal tailing pellets (Type 2) to that of the dried SMC. These could then be contrasted with the data gained for the parallel experiments in the fluidised-bed, to assess which would be preferable for the combustion of these fuels. Table 8.3 shows the conditions under which the packed-bed was run for each of these tests, including the amount of fuel used and the range of air flowrates.

CASE	PRIMARY AIR (kg/m^{2}hr)	SECONDARY AIR (kg/m^{2}hr)	AMOUNT OF FUEL (kg)
Combustion: Pellets	720 – 1200	480	6.26
Combustion: SMC	720	120 – 360	4.34
Gasification: SMC	0 – 480	0 – 600	3.5

Table 8.3: Conditions used in the two combustion tests and gasification in the packed-bed reactor.

8.4.3 Gasification in the Packed-Bed Reactor

SMC gasification was also completed in the packed-bed. As can be seen from Table 8.3, the overall amount of air (both primary and secondary air flowrates) was significantly lower for the gasification experiment, due to the fact that only partial oxidation was required, as described in Section 3.2.2. More air, and thus higher air ratios, was needed for the complete oxidation of the fuel during combustion.

8.4.4 Pyrolysis

For the pyrolysis experiment, the thermal degradation of the dried SMC, 0.3 kg of the material was placed in the primary fixed-bed. The heating rate of this section was kept constant at 10 °C/min, until a maximum temperature of 500 °C was achieved. The nitrogen flowrate used was 2.0 l/min.

8.5 DATA ANALYSIS AND EXPERIMENTAL ACCURACY

8.5.1 Data Analysis

Data concerning the temperatures, gas concentrations and solid/liquid residues, where formed, were analysed in various ways for the different tests. Each section below describes the information collected and the data manipulation performed for the numerous thermal treatments.

8.5.1.1 Data from the Laboratory-Scale Fluidised-Bed

During the combustion tests, the temperatures were monitored throughout the sand bed and freeboard using eight K-type mineral insulated thermocouples (T1-T8), the locations of which are shown in Figure 8.5 and Table 8.4. The tip of each thermocouple was located at the centre of the chamber.

THERMOCOUPLE	T1	T2	T3	T4	T5	T6	T7	T8
Height Above Plate (m)	0.11	0.20	0.31	0.42	0.56	0.76	1.54	1.74

Table 8.4: Locations of the eight thermocouples in the fluidised-bed.

The flue gas concentrations were also monitored. The exhaust gases passed through the cyclone to remove particulate matter and were then analysed, before being discharged to the atmosphere. The probe for measuring the gas concentration was located at the combustor exit, as indicated on Figure 8.5. The O_2, CO_2 and CO percentage concentrations were recorded using an online ADC MGA3000 series multigas analyser and data logger. Standardised gases were used to calibrate the analysers. The oxygen was measured via a chemical oxygen sensor, which worked on the principle that oxygen molecules were able to pass through the membrane to an electrolyte that initiated a reaction to produce a voltage proportional to its concentration. CO_2 and CO were measured using infrared absorption, which absorbs energy from the heated filament at different wavelengths. All species were recorded on a volumetric basis. Based on these gas concentrations, the combustion efficiency (η_{CE}) could be computed:

$$\eta_{CE} = \frac{\%CO_2}{(\%CO_2 + \%CO)} \times 100 \qquad (8.1)$$

where $\%CO_2$ and %CO were the concentrations of these gases in the exhaust (Llorente and Cuadrado, 2007). This is just one of many methods used for calculating the combustion efficiency; other techniques may take into account heat fluxes and/or the unburned carbon (Adanez, *et al.*, 2001; Gungor, 2008).

In addition, acid gas species were also analysed. These gas sampling probes were also located at the cyclone exit, where the gases passed through a glass wool filter, a water-cooled heat exchanger and a magnesium oxide drier before going to the analysers, which required dry, clean samples. NOx (NO and NO_2) were monitored using a Signal Series 4000 NOx analyser. Chloride (Cl^-) and sulphate (SO_4^{2-}) ions were monitored to indicate the presence of HCl and SOx and were collected via a wet chemical method followed by gas ion chromatography, in accordance with British Standard 1756, Part 4: 1977 (British Standards Institution, 1977c). This involved bubbling the gases through a 3 % hydrogen peroxide solution with a bromophenol blue ethanol/water indicator. Any Cl^- or SO_4^{2-} species present in the solution were detected using gas ion chromatography, which separated and identified such ions from the solution.

8.5.1.2 Data from the Packed-Bed Reactor

During the combustion and gasification tests in the packed-bed, the temperatures were monitored and the exhaust gas concentrations were recorded, as for the fluidised-bed tests described above. Additionally the

ash, which remained in the reactor after the thermal treatment of the material, was also analysed. Nine K-type mineral insulated thermocouples were used for the combustion tests, while seven were used during gasification. The tips of the thermocouples were situated at the centre of the chamber, as shown on Figure 8.12. The locations of these are given in Table 8.5 for combustion and Table 8.6 for gasification.

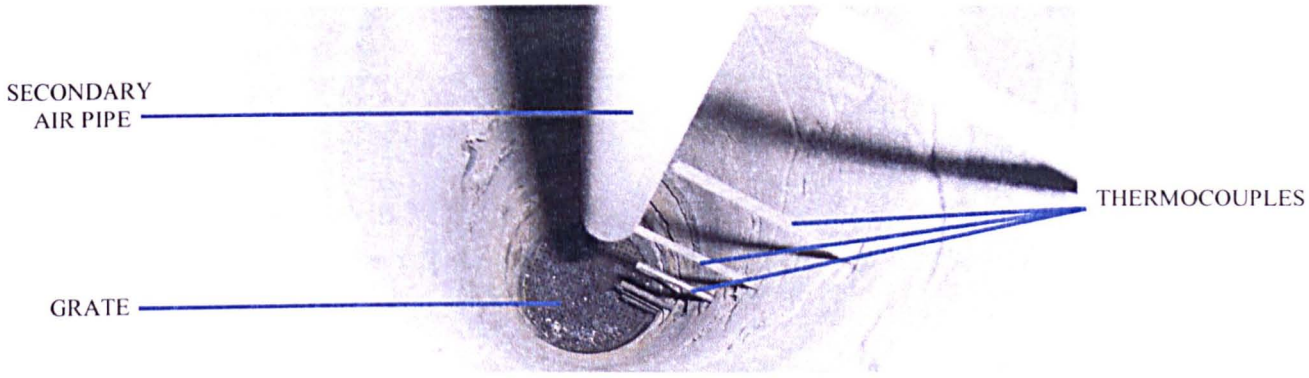


Figure 8.12: The inside of the reactor chamber in the packed-bed used for thermal treatment.

THERMOCOUPLE	1	2	3	4	5	6	7	8	9
Height Above Grate (m)	0.00	0.08	0.16	0.32	0.39	0.46	0.56	1.00	1.10

Table 8.5: Locations of the thermocouples in the packed-bed for combustion.

THERMOCOUPLE	1	2	3	4	5	6	7
Height Above Grate (m)	0.00	0.16	0.32	0.39	0.46	0.56	1.00

Table 8.6: Locations of the thermocouples in the packed-bed for gasification.

The exhaust gases were analysed (O_2, CO_2 and CO) using an online ADC MGA3000 series multigas analyser, from which the combustion efficiency (η_{CE}) was calculated, using Equation 8.1. The probe was located between T5 and T6, as shown on Figure 8.8. In addition, an ABB PGC Series 2000 analyser was employed during SMC gasification to measure the concentrations of fuel products. It has two columns to detect various species, including hydrogen and methane. From these data and the information gained from the weighing beam, key combustion parameters were calculated based on the methods outlined by Ryu, *et al.* (2006, 2007a,b). The main quantitative combustion parameters used to indicate the nature of the reaction processes can evaluate combustion performance. The mass loss, ignition front speed (IFS), ignition rate (IR), burning rates (BR) and equivalence ratio were compared between the cases. The first of these, the ignition front speed (in m/hr) is the value of the propagation of the ignition front with respect to speed, whereas the ignition rate (in kg/m^{2}hr) is with respect to mass, computed by:

$$IFS = H_o / \Delta t_i \quad (8.2)$$

$$IR = IFS \times \rho_o \quad (8.3)$$

where H_o is the initial height of the bed (in m), Δt_i is the length of the ignition propagation stage (in hrs) and ρ_o is the initial bulk density of the bed (in kg/m^3). ρ_o is defined as:

$$\rho_o = M_o / (A_{cross} H_o) \quad (8.4)$$

where M_o is the initial bed weight (in kg) and A_{cross} is the cross-sectional area of the reactor (in m^2). The ignition front propagation in a fixed-bed, such as that used here can be summarised schematically, as shown in Figure 8.13, where x is the coordinate and x_* is the moving coordinate, both in m.

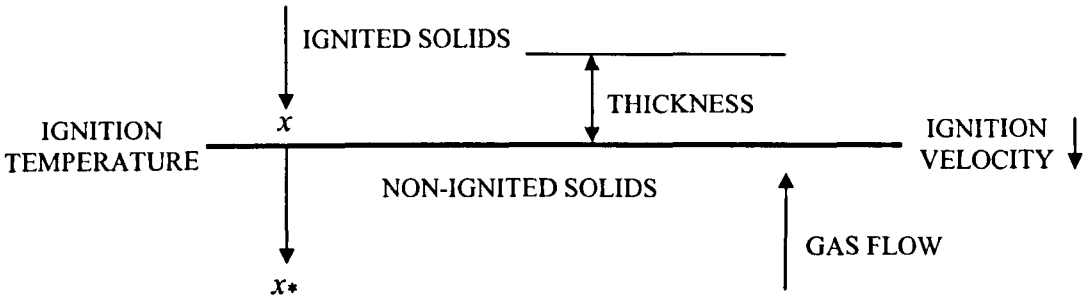


Figure 8.13: An overview of ignition propagation in a fixed-bed.
Source: Saastamoinen, *et al.* (2000)

The next two parameters concerned the burning rate – the first in the ignition propagation stage and the second in the char combustion or gasification stage (depending on whether oxidation is complete or partial), both of which have been found to be significantly and linearly influenced by the air flowrate. The ignition propagation period occurs at a higher burning rate than the char oxidation period (Ryu, *et al.*, 2007a,b). The burning rate in the ignition propagation stage (BR_i in kg/m^2hr) is computed by:

$$BR_i = \Delta M_i / (\Delta t_i A_{cross}) \quad (8.5)$$

where ΔM_i is the mass loss of the bed during the ignition propagation stage. BR_i is usually less than the IR, indicating that not all of the fuel is combusted as the ignition front passes; this allows char to remain, which is oxidised in the subsequent phase of the reaction. A similar expression is used to calculate the burning rate in the char oxidation stage (BR_c in kg/m^2hr):

$$BR_c = \Delta M_c / (\Delta t_c A_{cross}) \quad (8.6)$$

where ΔM_c is the mass loss of the bed in the char oxidation stage (kg) and Δt_c is the length of the char oxidation stage (hrs). Lastly, the equivalence ratio at the ignition propagation stage (λ_i) is defined as:

$$\lambda_i = m_{air,\,sto} / m_{air} \quad (8.7)$$

where:

$$m_{air,\,sto}\ (kg/m^2hr) = [\ 32\ (x+y/4-z/2)\ BR_i\ ] / [\ 0.233\ (18w+12x+y+16z)\ ] \quad (8.8)$$

for a fuel expressed as $w(H_2O)\cdot CxHyOz$, where m_{air} is the air mass flowrate (in kg/m^2hr), $_{sto}$ is stoichiometric (thus $\lambda = 1$), and w, x, y and z are coefficients for the empirical formula of the fuel, as expressed above. When these values had been calculated for all test cases, the percentage mass loss during ignition propagation, the ignition speed front, the average burning rate and the average equivalence ratio were compared to assess the differences in efficiency.

The appearance and composition of the ash residues collected were compared between the different cases. These were sent for elemental analysis, via the method overviewed in Section 6.2.3. Based on this, the

slagging (deposits within the furnace that are directly exposed to flame radiation, such as the boiler) and fouling (deposits where the cooling of the exhaust gases and flyash particles are not directly exposed to flame radiation) behaviour of the ash were investigated. The Alkali Index (AI) is an important threshold indicator of potential slagging and fouling, especially for biomass samples. This is conveyed by a simple index per unit of fuel energy (kg-alkali/GJ), where the composition of the fuel, especially its ash content and the quantity of alkali metals in oxide form (K_2O and Na_2O), are the key factors in determining the rate of fouling behaviour. This was calculated for each case using the elemental composition (data for the alkali metals sodium and potassium) of the flyash:

$$AI = (1 / Q)\, Y^a_f (Y^a_{K_2O} + Y^a_{Na_2O}) \tag{8.9}$$

where Q is the HHV or GCV of the fuel on a dry basis, in GJ/kg, Y^a_f is the dimensionless mass fraction of ash in the fuel, and $Y^a_{K_2O}$ and $Y^a_{Na_2O}$ are the dimensionless mass fractions of the K_2O and Na_2O present in the ash (Jenkins, *et al.*, 1998). Values for the probability of fouling have been calculated and are given in Table 8.7 below; all biomass fuels are prone to this as they tend to have relatively high quantities of alkali and alkali earth metals and thus their AI values are high; Si, Cl and S can also assist the formation of detrimental compounds, (Jenkins, *et al.*, 1998). AI values less than 0.17 kg-alkali/GJ indicate potential deposition problems, whereas values above 0.34 kg-alkali/GJ suggest fouling is certain; intermediate AI values mean that there is still a probability that slagging and/or fouling will occur. Whilst a number of indices are available to assess slagging and fouling due to specific components, these are often not appropriate for biomass fuels and as such, the AI is used here. Although this is not thought to be a comprehensive descriptive indicator when it comes to fouling behaviour, it is not necessarily an issue, as all biomass fuels tend to exhibit this behaviour (Jenkins, *et al.*, 1998). It has therefore recently been used as a predictive guide for fouling behaviour, particularly for biomass-based fuel sources. Ash samples with high AI values can also become agglomerated (Ryu, *et al.*, 2006). The presence of agglomerated ash from the thermal treatment of SMC may therefore be observed.

AI VALUE (kg-alkali/GJ)	PROBABILITY	EXAMPLES OF FUEL
< 0.17	potential fouling	wood (AI = 0.1)
> 0.17	probable fouling	RDF (AI = 0.2)
> 0.34	certain fouling	miscanthus (AI ≈ 0.34)

Table 8.7: AI values and their corresponding probabilities of fouling behaviour. Sources: Jenkins, *et al.* (1998); Ryu, *et al.* (2006)

8.5.1.3 Data from the Pyrolyser

The temperatures and gas concentrations were monitored using the methods previously described. Five K-type mineral insulated thermocouples were used to monitor temperatures in various locations; three thermocouples took readings at 200 mm, 250 mm and 300 mm from the top of the primary reactor (within and above the SMC bed) and a further two thermocouples recorded temperatures before and after the condenser (Figure 8.10). The compositions of the gaseous, liquid (pyrolytic oil) and solid (char) fuel

products were also analysed. The O_2, CO_2 and CO concentrations in the gas were determined using the ADC3000 analyser after passing through the condenser and condensing train. Furthermore, gas samples were taken at regular intervals and analysed using a Varian CP 3000 gas chromatograph to look for fuel products, such as hydrocarbons and other combustible gases. Ultimate analyses and CV tests, the methods of which were described in Section 6.2, were performed on the solid and liquid phase products.

8.5.2 Errors and Experimental Measurement Accuracy

8.5.2.1 Temperature Readings from Thermocouples

The K-type mineral insulated thermocouples used in all these thermal treatment tests had a temperature range of 0-1350 °C, with an accuracy of ± 0.75 °C; temperatures monitored did not exceed these values. The errors associated with this degree of accuracy were not problematic for the purpose intended here. The heating rate and maximum temperature during the pyrolysis of the SMC were set using the control box; these are thought to have a maximum error of ± 1 °C. During pyrolysis, the temperatures measured at T2 and T3, which were in the packed SMC bed, were likely to be between the temperature of the SMC and that of the surrounding gases, due to the radiation/convection balance at the tip of the thermocouple.

8.5.2.2 Gas Concentrations

The gases emitted from the exhausts of these reactors were passed through a glass wool filter before going to the online ADC MGA3000 gas analyser; as there was often a substantial amount of tubing required to connect the reactor to the analyser, there was likely to have been considerable time lags and potential leaks. The accuracy of the final readings also depended on the calibration gases used. The concentration of the gases in the calibration span gas cylinders is thought to produce an error in the readings of the exhaust gases of ± 4 %. In addition, a variety of other gas analysers were also employed. The Signal Series 4000 NOx analyser used during fluidised-bed combustion had an error of ± 0.2 ppm. The wet chemical method used to evaluate chloride and sulphate species had an accuracy of within 5 %. The ABB gas analyser for monitoring gas levels during gasification also had an accuracy of ± 4 %. The Varian CP 3000 gas chromatograph used for the analysis of fuel product gases from pyrolysis is thought to have an accuracy of ± 0.2 % but these were also dependent on the calibration gases used.

8.5.2.3 Gas and Air Flow Measurements

Rotameters were used to monitor the gas and air flowrates, where different sizes were employed depending on the magnitude of the flow, to minimise errors. For low flowrates, such as for the propane in the fluidised-bed, a small rotameter was used, ranging from 0 to 33.5 ± 0.5 l/min (80 ± 1.2 kg/m^{2}hr); large and medium rotameters were used for the primary and secondary air in the fluidised- and packed-beds, which ranged from 0 to 835 ± 1 l/min (2000 ± 2.5 kg/m^{2}hr) and 0 to 175 ± 1 l/min (420 ± 2.5 kg/m^{2}hr). The nitrogen flowrate into the primary fixed-bed reactor of the pyrolyser was controlled using a small rotameter, which ranged from 0 to 15 ± 0.25 l/min.

8.5.2.4 Weight Measurements

The weighing beam for the packed-bed was connected to a digital scale, accurate to the nearest 50 g. The weight measurements, however, could have been affected by the thermal expansion of the packed-bed, affecting the force at the connections when in use; the most accurate readings were thus taken before the reactor heated up and after it had cooled. It was therefore also necessary to weigh the initial material and collect and weigh the remaining ash using a more accurate balance (± 0.05 g) for all thermal treatments.

8.5.2.5 Errors in Data Manipulation and Calculations

In addition to the sources of error explored above concerning the accuracy of measurements and analysers, there would also be inaccuracies concerning the data manipulation. Many expressions (Equations 8.1 through 8.9) would contain errors, to a certain degree, which would be augmented by any further errors introduced with the data inputs. Sampling errors may also impact the results.

8.6 RESULTS AND ANALYSIS OF THERMAL TREATMENTS

This section presents and analyses the results of all the initial thermal treatment tests, including the combustion of the SMC-coal tailing pellets and SMC in both the fluidised- and packed-beds, as well as evaluating the gasification and pyrolysis of the SMC.

8.6.1 Combustion in the Laboratory-Scale Fluidised-Bed

Two tests were carried out to initially investigate the combustion of these materials in the fluidised-bed; SMC-coal tailing pellets (Type 1) were combusted and compared to the combustion of the raw SMC. The results of these tests are overviewed in Table 8.8 and Figures 8.14 and 8.15. 5 kg of pellets were placed into the hopper for the first test, whereas only 3 kg of SMC was loaded for the second; varying feedrates were used for both tests. Based on the correlation of the motor speed and the length of feeding time, 4.6 kg of pellets was fed into the fluidised-bed for the first test and 2.8 kg of SMC in the second.

PARAMETER		PELLETS	SMC
Fuel Feedrate (kg/hr)		1.7 – 5.7	1.7 – 3.9
Primary Air (kg/m^{2}hr)		240 – 610	190 – 770
Secondary Air (kg/m^{2}hr)		60	50 – 115
Average Gas Concentration	CO_2 (%)	13.50	12.91
	O_2 (%)	4.22	4.04
	CO (%)	1.22	1.38
	NOx (ppm)	8.8	-
	SO_4^{2-} (ppm)	0.52	-
	Cl^- (ppm)	0.61	-
Combustion Efficiency, η_{CE} (%)		91.74	90.31
Average Temperature (°C)	Bed	816	799
	Above Bed	813	797
	Freeboard	509	443

Table 8.8: Combustion conditions, gas concentrations, efficiency and temperatures for the preliminary combustion tests in the laboratory-scale fluidised-bed.

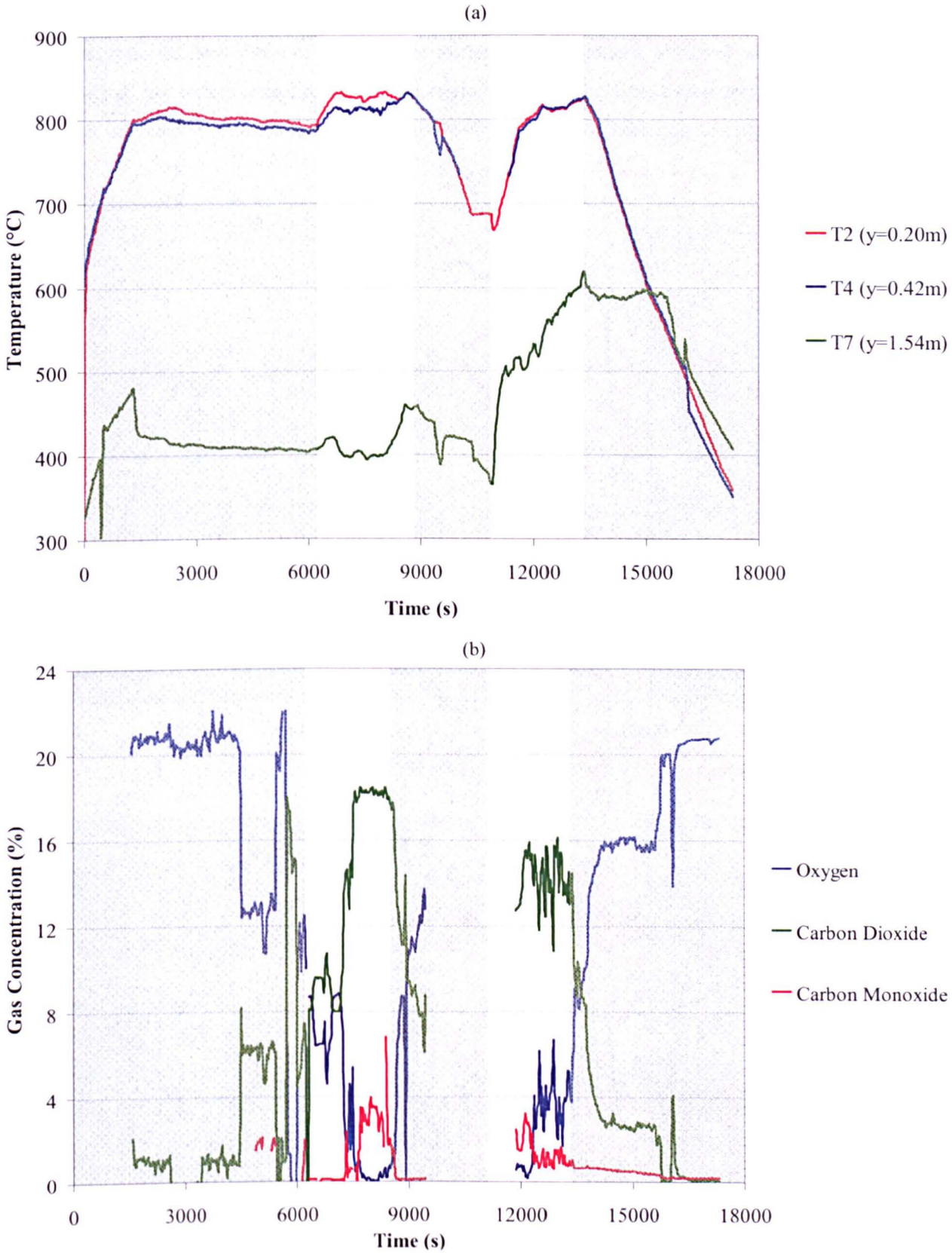


Figure 8.14: The results for pellet combustion in the fluidised-bed, showing (a) the temperature profiles; and (b) the gas concentrations at the exhaust. The shaded areas show where fuel feeding was not taking place.

Feeding was satisfactory at low mass feedrates (< 4 kg/hr at < 70 rpm), but at higher feedrates (> 4 kg/hr at > 70 rpm), there were problems and as such, there was a period where the equipment was down; due to this, there are gaps or anomalies in the data readings for the temperature profiles and gas concentrations.

Once the feeder was blocked and the fuel stopped feeding, the temperatures started to decrease significantly, particularly those of the bed and in the lower freeboard, although when the problem had been rectified, the burner was briefly ignited again to reheat the bed; this increased the temperatures throughout the reactor, with the maximum around 800 °C before fuel feeding was recommenced.

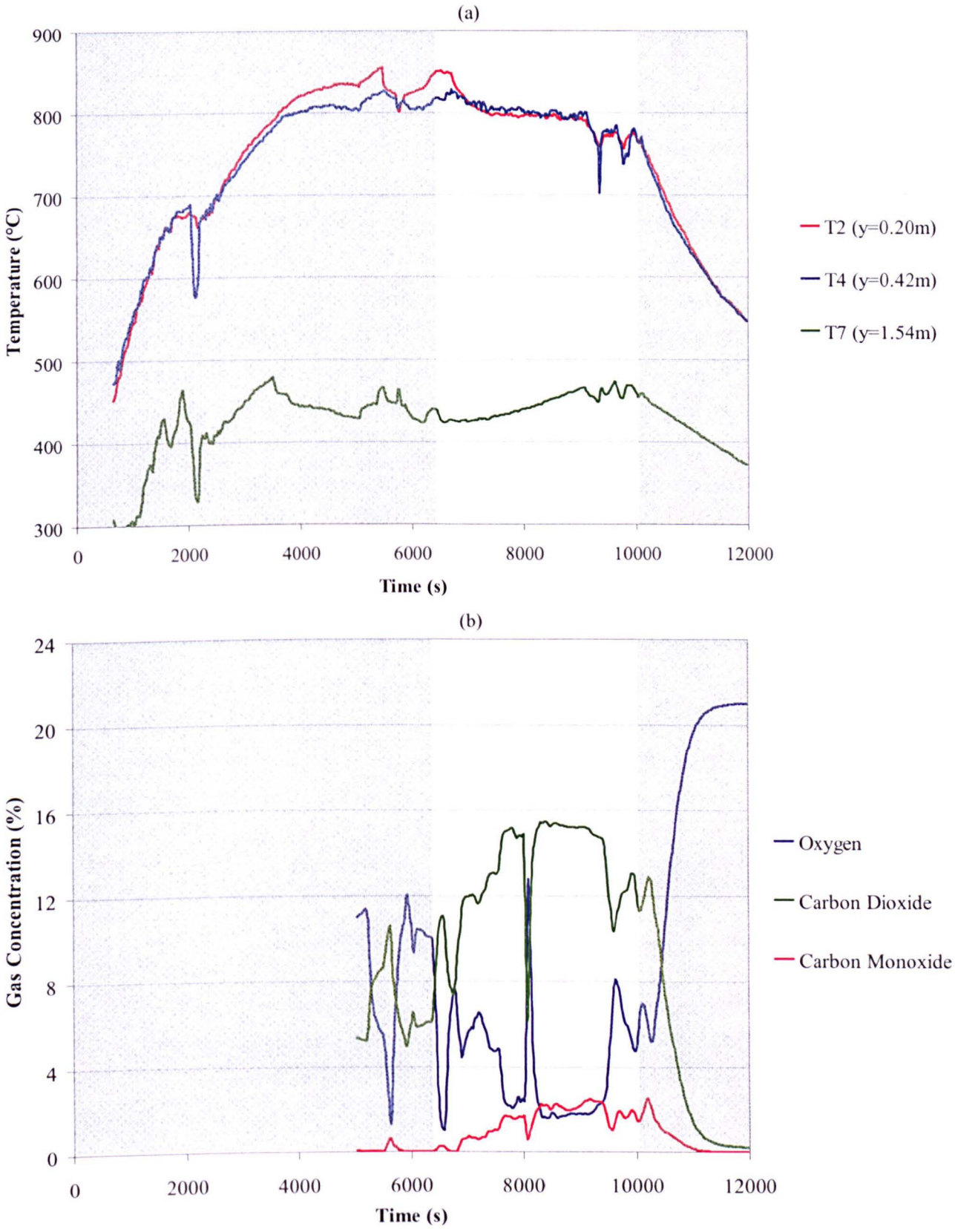


Figure 8.15: The results for the fluidised-bed combustion of SMC, showing (a) the temperature profiles; and (b) the gas concentrations at the exhaust. The shaded areas show where fuel feeding was not taking place.

Although the temperatures were monitored at eight locations, the profiles here focus on three main thermocouples. T2 was located in the bed (at y=0.20 m), T4 was located just above the bed (at y=0.42 m) and T7 near the top of the freeboard (at y=1.54 m). When the bed reached a stable temperature, around 800 °C, fuel feeding was initiated. On the introduction of fuel into the reactor, the temperatures above the bed became slightly elevated in both cases, but remained fairly stable during the later combustion stages. Where fuel feeding stopped due to the blockages, the temperatures decreased, as indicated. The gas concentrations were monitored and the trends were shown in Figures 8.14 and 8.15 for these tests. During the combustion periods, where fuel feeding was occurring (the non-shaded areas on the graphs), O_2 was low, whereas the CO_2 was high, as expected. CO concentrations were generally low, even during combustion, indicating primarily complete combustion, where most C was fully oxidised, as indicated in Equation 3.2. The combustion efficiency was calculated based on these concentrations; pellet combustion was slightly more efficient, where η_{CE} = 90.96 %. η_{CE} for SMC combustion was 89.66 %. Acid gases were also measured during pellet combustion; average values were given in Table 8.8. NOx concentrations were low, despite the abundant N in the initial material, particularly in the SMC substrate; as such, gas cleaning, discussed in Section 3.4, is unlikely to be required, providing this is representative. The SO_4^{2-} in the flue gases, an indicator of the SOx that form, was very low, as was the chloride concentration; the concentrations of S and Cl in the feed materials was also notable. The reasons for this, the inorganic origins of such species, were considered previously, with reference to Williams (2001), Williams, *et al.* (2001a) and Chugh and Patwardhan (2004); the results herein appear to corroborate these.

8.6.2 Combustion in the Packed-Bed Reactor

The fuel was placed in the packed-bed until a depth of approximately 0.45 m was reached; this equated to 6.26 kg Type 2 pellets for the first test and 4.34 kg of SMC for the second. The remaining mass after the combustion tests, comprised of ash, was 1.7 kg for the pellets and 1.1 kg for the SMC. SMC combustion took approximately half the time of pellet combustion reflecting the superior CV and energy density of the pellets compared to the raw fuel. Average results from these tests are compared in Table 8.9.

PARAMETER		PELLETS	SMC
Amount of Material (kg)		6.26	4.34
Primary Air (kg/m^{2}hr)		720-1200	720
Secondary Air (kg/m^{2}hr)		480	0-480
Average Gas Concentration (%)	CO_2	17.28	17.19
	O_2	0.49	2.76
	CO	1.85	5.22
Combustion Efficiency, η_{CE} (%)		90.3	76.7
Average Bed Temp. (°C)		1139	1133

Table 8.9: Conditions, gas concentrations and efficiency for the preliminary tests in the packed-bed.

Pellet combustion in this reactor was far superior; the high CO concentrations during SMC combustion resulted in a marked reduction in efficiency of around 14 %. There was a significant amount of excess oxygen in the system, which was not used during SMC combustion, thus the partial oxidation reaction of

Equation 3.2 was more dominant. Despite this, the temperatures for both cases were high, reaching similar average temperatures in the bed. The temperature profiles, mass loss and gas concentrations for these experiments are shown in Figures 8.16 and 8.17 for pellet and SMC combustion.

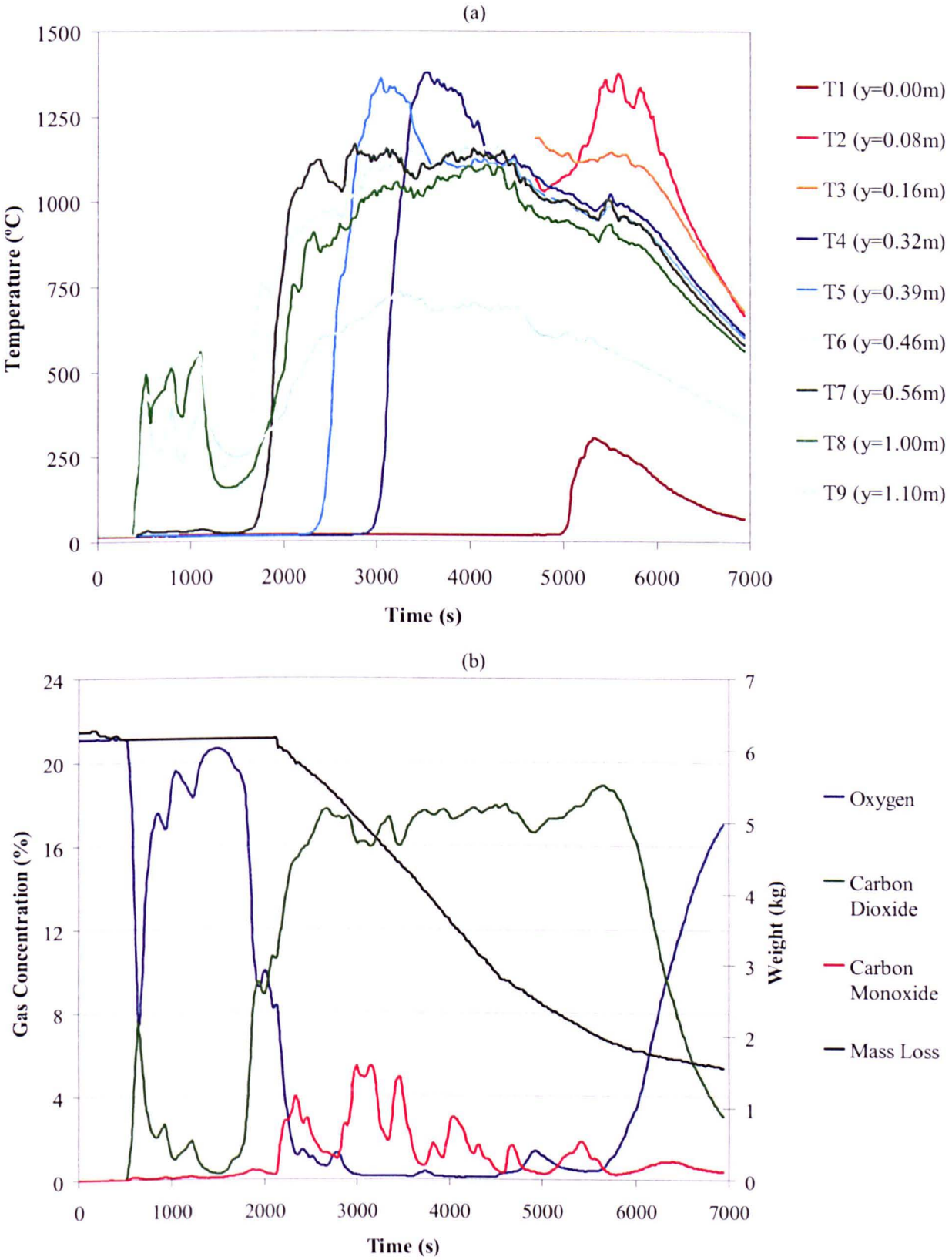


Figure 8.16: The results for the packed-bed combustion of SMC-coal tailing pellets, showing (a) the temperature profiles; and (b) the gas concentrations at the exhaust and the mass loss.

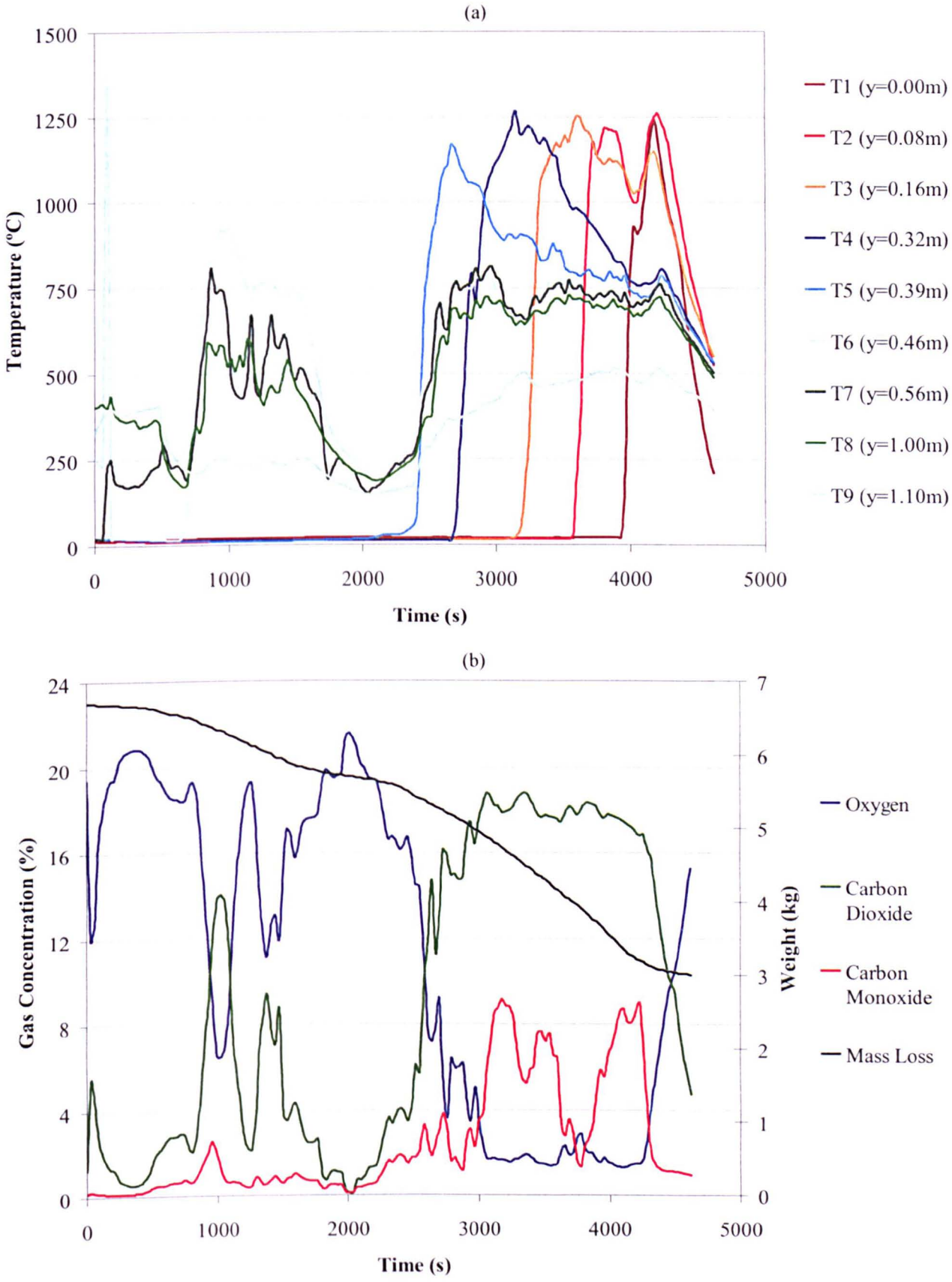


Figure 8.17: The results for the packed-bed combustion of SMC, showing (a) the temperature profiles; and (b) the gas concentrations at the exhaust and the mass loss.

The temperature profiles for the first part of both graphs are quite erratic, as this period was used to ignite the burner and adjust the air flowrates. The primary and secondary air flowrates were not kept constant,

but modified to ensure that the combustion of the fuel took place; this is considered further below. Once the ideal flowrates were reached, the combustion proceeded to completion. The propagation of the flame through the fuel was very stable and is represented clearly by the way the temperatures of subsequent thermocouples increase, particularly for the SMC combustion, even though the bed temperatures were similar. After the temperature peak of T1 in the reactor grate, the temperatures began to drop, as the reactions slowed. The maximum temperatures reached were significantly higher for pellet combustion, again due to their higher CV; the temperatures for SMC, however, were not vastly dissimilar, proving the material is capable of being used as a fuel on its own, the CV is high enough to combust in a self-sustaining manner and it can produce temperatures that are sufficiently high for power production.

The O_2 concentration was initially high and the CO and CO_2 concentrations low, as little combustion was taking place. Once combustion was fully initiated, O_2 decreased and the combustion products began to form; this is also where the onset of mass loss occurred and the temperatures became significantly elevated. Once the reaction was near completion, O_2 became more abundant and CO and CO_2 significantly decreased, as the rate of combustion product formation slowed. The above figures also show the weight loss due to fuel combustion throughout the duration of the experiments. When combustion was initiated, the mass decreased steadily, representing stable combustion. The primary and secondary air flowrates had to be manipulated to achieve proper combustion, as initial combustion was very uneven, particularly for the SMC (Figure 8.18). Furthermore, the air flowrates are crucial in determining whether or not a fuel will burn, and thus optimum conditions are required for this. If the air flowrates are too high, this can cause dramatic cooling of the reaction and combustion will cease, whereas if the flowrates are too low, there may not be enough oxygen for the reaction to continue or be completed; this was more pronounced for the SMC. The gas concentrations were monitored to ensure complete combustion was achieved: specifically, high CO_2, with low CO and O_2.

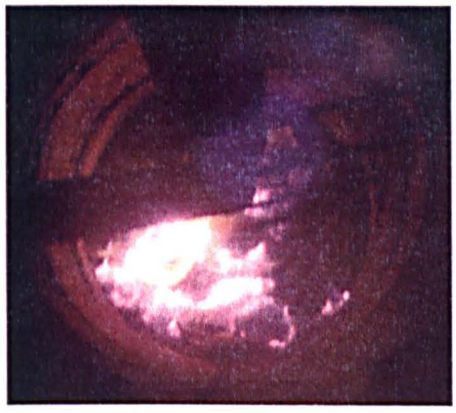


Figure 8.18: Uneven combustion of the raw SMC in the packed-bed.

The ash residues remaining at the end of these tests are shown in Figure 8.19. As shown, this was mainly in the form of fine powdered ash, although for pellet combustion, some ash had been sintered by the heat of the reactor. The composition of the material was analysed and the AI computed using Equation 8.9; these were compared to that of the SMC gasification. These are considered presently.

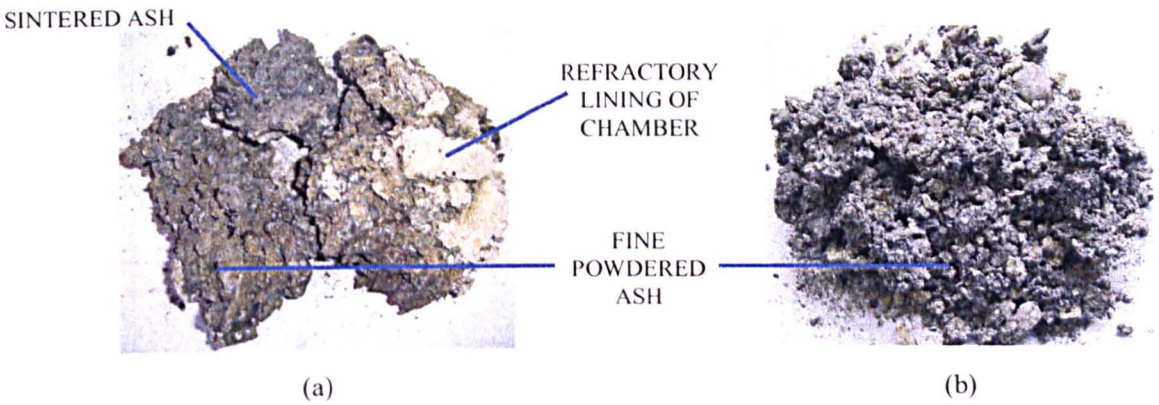


Figure 8.19: Photographs of the ash from (a) SMC-coal tailing pellet combustion and (b) SMC combustion in the packed-bed.

8.6.3 Gasification in the Packed-Bed Reactor

3.5 kg of dried, unpelletised SMC was placed into the packed-bed, a depth of 0.4 m. Once gasification was complete, 0.9 kg of ash remained. Even though significantly less material was used, the reaction took approximately the same amount of time as the pellet combustion, as gasification occurs more slowly.

Fairly high temperatures are required for gasification to occur, usually over 800 °C. As can be seen from the temperature profiles (Figure 8.20), the temperatures only reached this value towards the end of the reaction at the bottom of the reactor, showing that true gasification only occurred on the grate. This implies that there was not enough heat to generate the necessary reactions, and thus conditions were not entirely appropriate. To improve this, the air flowrates were modified several times over the course of the test. It was found that if the air flowrates were low, not enough heat was generated, leading to the specific problem just discussed. However, if the air flowrates were too high, SMC combustion reactions predominated, instead of gasification. A recommendation for the future would be to introduce pre-heated air, thus generating the temperatures required but at the low air flowrates needed to limit full oxidation. Another reason why true gasification is thought not to have occurred properly is that the proportion of CO present in the exhaust was quite low for most of the reaction, whilst CO_2 was abundant (Figure 8.20); higher percentages of CO were not seen until the latter stages, as the reactor reached a significantly high temperature, discussed above. As CO_2 was relatively high for most of the reaction, this indicates that full rather than partial oxidation was taking place, as illustrated in Equations 3.3-3.5.

The mass loss curve clearly shows two distinct phases, as identified on Figure 8.20b, where the slope of the curve changes. The first phase is ignition propagation, where the initial drying of the material occurs followed by pyrolysis. During this stage, the flame gradually ignited the SMC, propagating downwards through the material until it reached the bottom of the chamber. At this point, the char had been formed and then gasification began, as indicated on the graph. The char gasification stage was initiated at the point where the CO concentration started to rise, and was completed when the CO concentration decreased rapidly. Once the gasification of the char occurred, only ash remained.

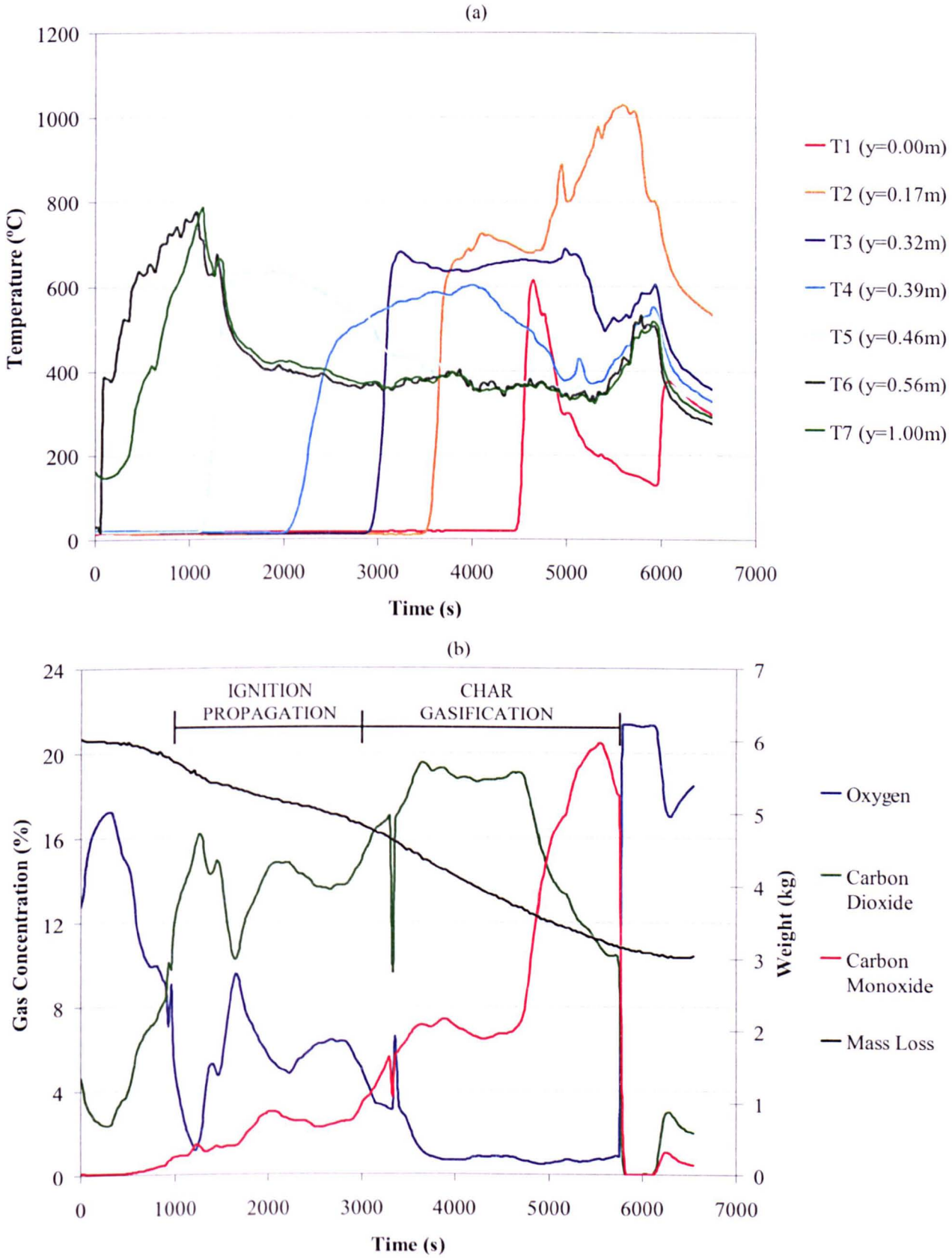


Figure 8.20: SMC gasification – (a) the temperature profiles; and (b) the gas concentrations and mass loss.

In addition to these gases, others products of gasification were monitored using the ABB analyser; these included hydrogen, methane, hydrogen sulphide and carbonyl sulphide concentrations (Table 8.10). The concentrations of H_2 and CH_4 were generally low, although the brief peaks during the ignition

propagation phase were quite high. As these are both combustible, they can be used as fuel products from this process. This shows that some gasification took place, as these are unlikely to be contained in the exhaust gases from combustion reactions in such quantities, as they would be consumed rapidly after they were formed. These products form via the mechanisms outlined in Equations 3.4 and 3.5. The H_2S and COS both had limited concentrations, which peaked towards the end of the char gasification stage.

GAS CONCENTRATION (%)	H_2	CH_4	H_2S	COS
Average	13.26	2.08	0.02	0.02
Maximum	29.14	7.66	0.04	0.09

Table 8.10: Gaseous fuel concentrations for SMC gasification in the packed-bed.

8.6.4 Pyrolysis

300 g of non-pelletised SMC was placed into the primary fixed-bed reactor of the pyrolyser; once the maximum temperature of T3 = 500 °C was reached, the pyrolyser was held at this temperature for an hour, to ensure the pyrolysis of the material. The temperature profiles for all 5 thermocouples are shown below (Figure 8.21). T3, the thermocouple closest to the top of the reactor (200 mm from the top) had the highest temperature throughout; temperatures gradually decreased further down the reactor and into the SMC contained within it (T2 = 250 mm and T1 = 300 mm from the top). The temperature difference between the two sides of the water-cooled condenser was clear (T4 and T5). The gases analysed are also shown in Figure 8.21; as expected, CO was much higher than for combustion reactions, as pyrolysis is thermal decomposition and not an oxidation process. Despite the lack of oxygen fed into the system, CO_2 was still produced in significant quantities; this may be due to the oxygen from the SMC (~20 %).

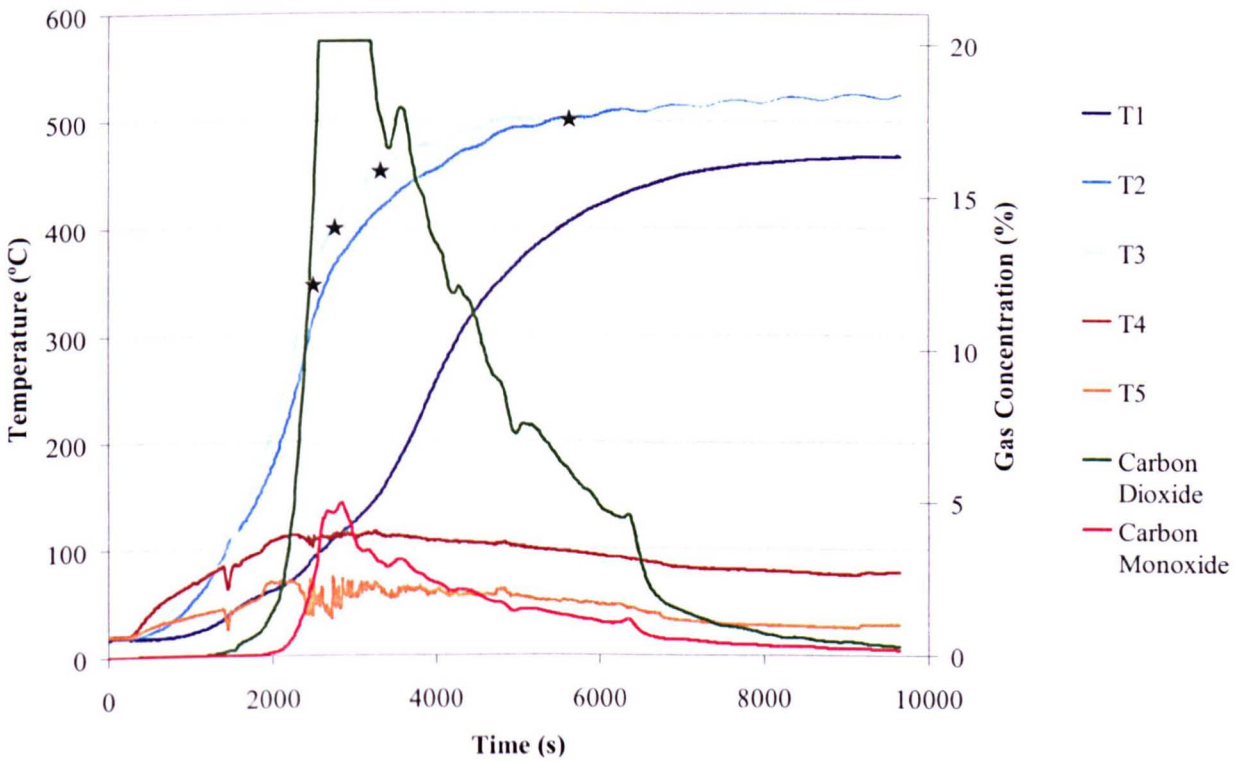


Figure 8.21: Temperature profiles and transient exhaust gas concentrations from the pyrolysis of SMC. ★ show where the gas samples were collected from the absorption tower.

In addition to these, other gases were also analysed, including hydrogen and various hydrocarbons, using gas chromatography. Fuel gas formation from pyrolytic reactions was delineated in Equation 3.8. The exhaust was passed through the absorption tower and collected in four tubes, when specific temperature readings were gained for T3, as identified on Figure 8.21. The results for this analysis are shown in Table 8.11. Towards the end of the reaction, the proportion of hydrocarbon fuels increases; the percentages of methane, ethane and propane all become more abundant as the temperatures inside the reactor became higher. The amount of carbon monoxide during this reaction was quite high, as already suggested by the readings from the other gas analyser. As this happened, the trend with the concentration of carbon dioxide – a product of combustion – was shown to decrease.

GAS	GAS CONCENTRATION (%) WITH TEMPERATURE			
	350°C	400°C	450°C	500°C
CO_2	13.02	16.61	14.44	8.19
CO	8.96	9.40	6.67	7.69
CH_4	0.11	0.54	0.78	1.26
H_2	0.04	0.08	0.22	1.34
C_2H_4	0.14	0.08	0.13	0.18
C_3H_8	0.06	0.05	0.07	0.08

Table 8.11: Proportions of the total fuel product gases with temperature variation, from SMC pyrolysis.

The initial weight of the SMC sample was 300 g, which produced a total char yield of 130 g (43.33 %). The weight differences of the bottles, tubing and absorption tower of the condensing train are presented in Table 8.12; the liquid (pyrolytic oils) produced weighed a total of 104 g (34.71 %), thus the remainder, 65.88 g (21.96 % by difference), left the system as either gaseous products or was lost as waste.

COMPONENT	INITIAL WEIGHT (g)	FINAL WEIGHT (g)
Sample Weight	300	130 (char yield)
Liquid Yield – Bottle 1	273.48	361.70
Tubing Between Bottles 1 & 2	226.55	229.73
Liquid Yield – Bottle 2	237.60	240.75
Liquid Yield – Bottle 3	382.00	390.93
Absorption Tower	531.10	531.74

Table 8.12: Results of the weight differences for various components of the pyrolyser.

The composition of the char and liquid produced by this processing were analysed. The ultimate analyses and CV results are shown in Table 8.13. The char formed via the reaction outlined in Equation 3.7, was similar in appearance, in terms of particle size and shape, to the original material; once pyrolysed, however, the material became dark and uniform in colour (Figure 8.22). There were high proportions of C and O; the initial C content of the SMC was similar to that recorded for the char, although the proportion of O had increased significantly. The amounts of H and N conversely decreased slightly compared to the raw material. The CV of the char was quite significant, although was lower than that of the raw material as some energy content had been removed to form the pyrolytic liquids and the gas phase fuel components.

As can be seen from Figure 8.22, some SMC particles from the reactor were entrained in the gases and became deposited in the first condensing bottle, contained within the pyrolysis liquid. This liquid had a high O content and a low CV. The liquids produced, however, were clearly different and separated out in the container; the heavier, paler pyrolysis liquid settled towards the bottom of the container, with the darker liquid (aqueous phase) on top. The CV tests were completed separately for these two substances and large differences were found between their energy values; the paler pyrolysis liquid had a much higher CV of 5.85 MJ/kg, whereas the darker, aqueous phase has a very low CV of just 2.16 MJ/kg. The darker, lower CV product was found in greater abundance however, which was why the overall CV for the liquid phase was low. Separation of these two liquid phases may be beneficial and further processing, such as refining of these may be required.

ANALYSIS	CONSTITUENT	CHAR	PYROLYTIC LIQUID
Ultimate Analysis (%)	Carbon	34.2	5.0
	Hydrogen	1.2	11.8
	Nitrogen	1.4	1.5
	Oxygen	63.2	81.8
CV (MJ/kg)	GCV	7.95	2.98
	NCV	7.68	-

Table 8.13: The ultimate and CV analyses of the char and pyrolytic liquid produced from SMC pyrolysis.

Figure 8.22: The char and pyrolytic liquid from the pyrolysis of SMC.

8.7 FURTHER ANALYSIS AND DISCUSSION OF RESULTS

8.7.1 Fluidised-Bed Combustion

As can be seen from the results of the fluidised-bed combustion of these wastes, the thermal treatment of the pellets performed far better than that of the SMC. The combustion efficiency was greater for pellet combustion and, as such, the temperatures were significantly higher, particularly those in the freeboard, due to the greater energy density of the pelletised fuel and also their higher energy content (from additions of the coal tailings). Furthermore, the increased bulk density of the pellets compared to the unpelletised fuel meant that the fuel burnt within the bed, also meaning that the temperatures would be higher here. It is likely that the light SMC particles may have been entrained in the gas and escaped with the flue, without being burned. The data concerning pellet combustion in a fluidised-bed, coupled with the results from the parallel experiments in the packed-bed indicate that the combination of these fuels in

pelletised form is superior to that of the SMC, for a variety of reasons. Combustion of both the fuel pellets and the SMC was more efficient in the fluidised-bed, thus this reactor would seem preferable.

8.7.2 Comparison of Thermal Treatments in the Packed-Bed

Table 8.14 summarises the key parameters calculated using the equations from Section 8.5.1.2 for the two combustion cases (Pellets and SMC) and SMC gasification (G). Direct comparisons can be made as the same reactor was used and accordingly, the values computed herein have been compared to those of:

- Ryu, *et al.* (2006) for miscanthus pellets (Mp), pine cubes (Pc), willow (Ww) and RDF pellets,
- Ryu, *et al.* (2007a) for cardboard (Cb)
- and Gilbert, *et al.* (2009) for switchgrass pellets (Sp) and raw switchgrass (Sr).

	PARAMETER								
TEST	**ΔM_i (%)**	**IFS (m/hr)**	**IR (kg/m^2hr)**	**BR_i (kg/m^2hr)**	**BR_c (kg/m^2hr)**	**$\bar{x}$ BR (kg/m^2hr)**	**λ_1**	**AI (kg-alkali/GJ)**	**ρ (kg/m^3)**
Pellets	51.4	0.7	296.4	152.5	75.9	109.8	1.27	0.17	442.8
SMC	19.4	1.3	376.8	72.9	120.4	93.7	0.45	0.13	300.3
G	28.00	0.65	180.66	50.59	61.37	54.83	0.96	0.18	278.5
Mp	75-81	0.36	-	-	-	94-148	2.1-2.3	~0.34	660
Pc	84-86	0.7-0.8	-	-	-	123-134	2.1-2.3	<0.1	272-295
Ww	68-82	1.1-1.2	-	-	-	104-141	2.9-4.1	<0.1	181
RDF	73-75	0.2-0.3	-	-	-	97-112	2.2-2.4	>0.2	715
Cb	68-90	-	190-300	135-310	55-115	-	2.0-2.5	-	76
Sp	90	0.76	280	312	-	252	2.39	-	370
Sr	65.6	8.9	508	385	-	253	2.40	-	57

Table 8.14: Table of key parameters defining the thermal treatments in the packed-bed, compared to those of other studies (Mp, Pc, Ww, RDF, Cb, Sp and Sr). The average burning rate ($\bar{x}$ BR) was based on the mass loss during the entire period.

The two combustion cases show that the mass loss during ignition propagation was much higher for the pellets, compared to the unpelletsied SMC, and as such, the burning rate during this phase was much higher. By contrast, the burning rate during char combustion was greater for the SMC, although the overall burning rate was faster for the pellets. The ignition front speed and the ignition rate for the pellets were significantly lower than for the SMC, reflected by the difference in densities. Comparisons made between the pelletised and non-pelletised fuels in this study have been confirmed by the differences between the pelletised and non-pelletised switchgrass of Gilbert, *et al.* (2009), namely the mass loss during ignition propagation, the ignition front speed and the ignition rate. The SMC combustion and gasification cases can also be compared. Mass loss during ignition propagation was higher for SMC gasification, compared to its combustion. In contrast with the above comparison, the burning rates do not follow the above trend as only partial combustion was occurring during gasification; this is true of all three burning rates computed. Even though very similar densities are found in the SMC used for the combustion and gasification reactions, the differences in air flowrates and thus in the reactions and the speed at which they occurred are clearly reflected in the ignition front speed and the ignition rate.

In general, as discussed above, these results corroborate well with other combustion tests of biomass samples. The mass loss during ignition propagation however was significantly lower for the tests here, compared to the results gained by Ryu, *et al.* (2006, 2007a) and Gilbert, *et al.* (2009); the majority of mass loss occurred during the char combustion phase for the materials herein, particularly for SMC combustion and gasification, thus the char formation, rather than combustion, is a significant process occurring during the initial stages of these reactions. As previously suggested, the BR_i was lower than the ignition rate in all cases here, thus char remained to be combusted after volatile combustion. The ignition front speeds were similar for all the cases shown in the table, except for the raw switchgrass (Gilbert, *et al.*, 2009); this is likely to be due to the very low density of the material. This was also found to be the case for the comparison of pellet combustion and SMC combustion, as the densities and the ignition front speeds also show a negative correlation. Although the range of ignition rates is vast for the previous literature, the results gained here are generally comparable and are within the range shown. The burning rates for the pellet combustion test herein and those of Ryu, *et al.* (2006, 2007a,b) are quite analogous; the results achieved by Gilbert, *et al.* (2009), however, show much higher overall burning rates, although the results for Sp and Sr were similar. The burning rates for the gasification test should be significantly lower than the combustion cases, as supposedly little complete combustion was taking place – only partial oxidation is expected during gasification reactions. The equivalence ratio at ignition propagation (λ_i) was also calculated for each case. These values are significantly lower than those reported for other materials. Ryu, *et al.* (2007a,b) state that this is the average stoichiometry required for the reaction to occur, which is represented as the ratio of the actual fuel-oxidant ratio to the stoichiometric ratio. This suggests that less oxygen is required to combust or gasify the pellets or the SMC in the packed-bed.

The main elements found in the raw materials, determined in Chapter 6, included Ca, S and K, the latter of which contributes to slagging and fouling. The Na content of the ash is also a part of the cause of this. The elemental analysis of the ash samples are shown in Table 8.15.

ELEMENT	AMOUNT (mg/kg)		
	PELLET COMBUSTION	SMC COMBUSTION	SMC GASIFICATION
Alkali Index (kg-alkali/GJ)	0.17	0.13	0.18
Al	31800	13000	15000
Ca	70550	359000	302000
Fe	18300	10000	11000
K	11600	26500	35000
Mg	6875	18600	19900
Mn	395	772	1020
Na	1950	4460	5530
P	6355	18800	24400
S	8535	25700	35800
Si	4690	3090	3760
Sr	240	540	640
Ti	1100	609	714
Zn	98	1840	2750

Table 8.15: Composition and properties of the ash residues from the thermal treatments in the packed-bed.

The Alkali Index was calculated from these results, assuming that all K and Na present were in oxide form. From these values, it can be seen that fouling is probable with pellet combustion in the packed-bed and with SMC gasification, as these values were equal to or greater than the 0.17 kg-alkali/GJ threshold described previously. SMC combustion in the packed-bed still had the potential to foul, as there were noteworthy amounts of the two required metals in the ash. Of the other elements that were particularly prominent in the raw materials, the Ca appears to be more concentrated in the ash samples, especially where only SMC was used, as this metal is found in significantly larger concentrations in the SMC. The SMC substrate initially had high quantities of S, which has remained in the ash for the packed-bed combustion and the gasification; this is beneficial in terms of reduced SOx emissions. Again, there are higher S concentrations in the two tests were only the SMC was thermally treated.

8.7.3 Gasification and Pyrolysis

Gasification was not successful, as the reactions were cooled if there was not enough air in the reactor, which meant that the temperatures generated were not sufficient to initiate gasification reactions. If there was excess air in the system, combustion reactions were dominant. Pyrolysis did produce a wide range of potential fuels, in solid, liquid and gaseous forms, but as seen from their CV above, the energy contents of these were generally low, although these could have a variety of further uses, providing they are managed effectively. These thermal treatments are thus thought not to be as suitable for these wastes.

8.8 SUMMARY OF RESULTS AND CONCLUSIONS FROM THE INITIAL THERMAL TREATMENT TESTS

The materials were pelletised on a mass scale, then used in a series of thermal treatments to compare the efficiencies of these to non-pelletised SMC in fluidised- and packed-beds. Additionally, SMC pyrolysis and gasification were performed; these were by contrast, not as successful. Pellet combustion in both reactors, although in particular in the fluidised-bed, was very successful. The emissions (NOx, SOx and HCl) did not appear to be problematic, as previously suggested. SMC combustion in the fluidised-bed was also successful, where high temperatures were maintained and emissions were comparable to pellet combustion. By comparison, SMC combustion in the packed-bed was not as efficient. The combustion parameters calculated for the packed-bed tests were generally comparable to those for other biomass fuels, particularly the ignition front speed, and the ignition and burning rates; the equivalence ratios were somewhat lower than the other values reported. Although considerable amounts of ash were produced, this can be used as an activator for PFA in the cement industry, as Russell, *et al.* (2005) suggests.

Based on the results from these preliminary tests, it has been recommended that as the fluidised-bed combustion of SMC-coal tailing pellets was most successful, this warrants further investigation and will consequently be the focus of additional experimental work for this PhD. This is also preferred for high ash content fuels, such as these. This will in particular focus on enhancing the combustion efficiency through manipulating variables and assessing the pollutants that are formed, both gaseous and solid.

9

FLUIDISED-BED COMBUSTION OF FUEL PELLETS

9.1 INTRODUCTION

As seen from the previous chapter, the combustion of the SMC-coal tailing pellets in the laboratory-scale fluidised-bed performed better, achieving higher combustion efficiencies than the combustion of the SMC alone and the other thermal treatments. This was due to the pellets having a superior CV from the additions of the coal tailings, as well as the greater bulk and energy densities resulting from their pelletisation. This greater density allows combustion to take place in the heated sand bed, which directly improves the energy efficiency by minimising the small particles that escape unburned with the flue gases (Saenger, *et al.*, 2001; Holm, *et al.*, 2006). As a result, this was chosen as the main thermal treatment and thus was the focus of the succeeding experimental stage. A series of tests were devised and performed to assess alterations of three key parameters: the primary air flowrate, the pellet feedrate and the sand bed depth, with the aim of determining the optimum combustion conditions for these wastes in this combustor; these results are presented here. The manipulation of these variables were thought to influence the temperatures achieved throughout the reactor, the gas concentrations, the pollutant species produced and the overall combustion efficiency, as well as the properties and composition of the flyash.

Additionally, combustion tests were performed where the pellets contained 1 wt% of either the caustic soda or starch binder, to assess the impacts of these on the combustion behaviour and the pollutants formed. These were utilised as binders to improve pellet quality, detailed in Section 7.6 and 7.7. This was vital, as any additives used in fuel pellets need to have a minimal impact on their combustion.

9.2 MANIPULATING THE COMBUSTION VARIABLES IN THE LABORATORY-SCALE FLUIDISED-BED

9.2.1 Description of Modified Analytical Set-Up

The laboratory-scale fluidised-bed used for these tests was described in detail in the previous chapter – Section 8.3.1. The analytical set-up used for the additional experiments was similar, where temperatures were measured at eight locations throughout the bed and freeboard (at the locations outlined in Table 8.4) and gas concentrations (O_2, CO_2, CO and NOx) were monitored at the exhaust. As before, the flue gas was also analysed for other acid gas species (sulphates and chlorides) and gas samples were taken at four locations throughout the reactor, from samples ports, as indicated on Figure 9.1, for further gas analysis. In addition, the flyash was also collected in the cyclone and later analysed.

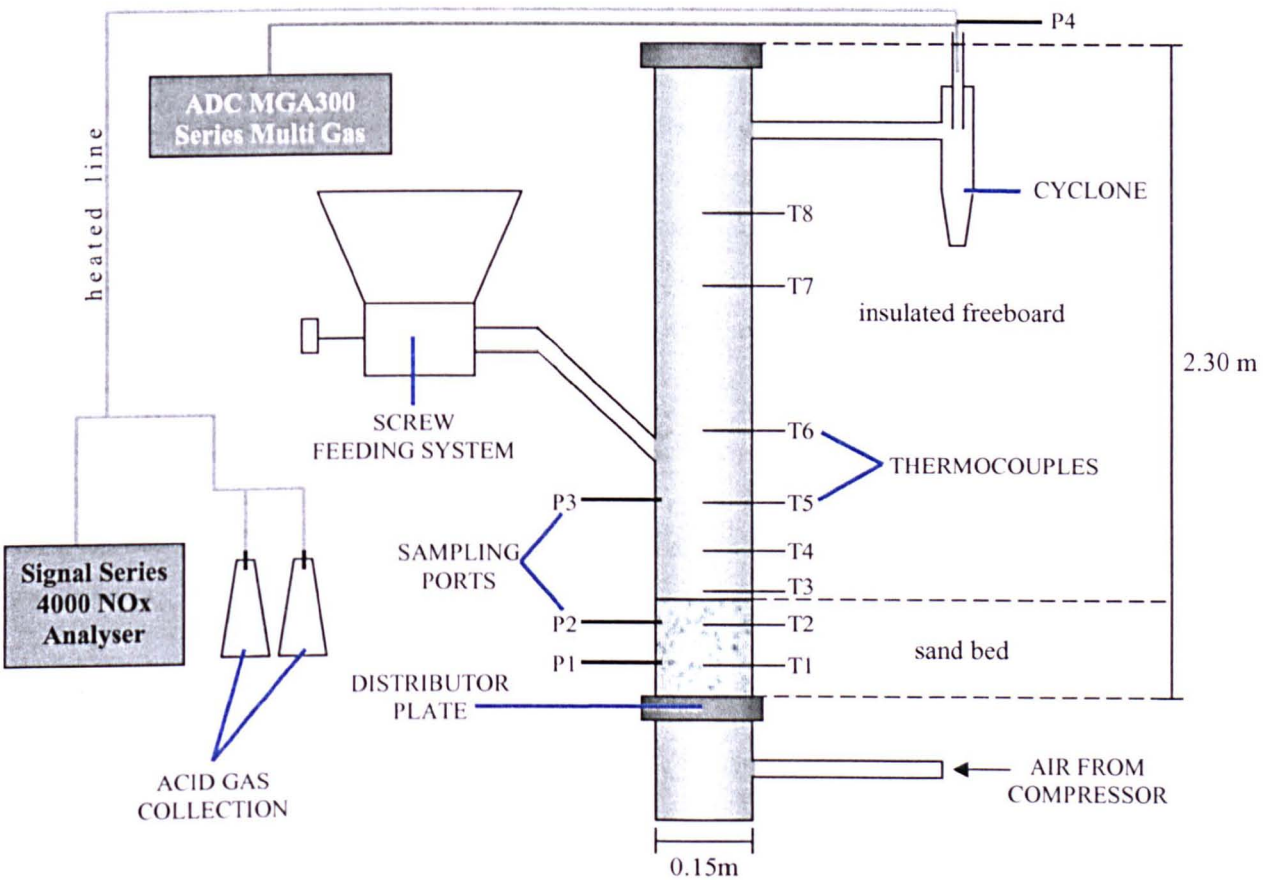


Figure 9.1 The modified fluidised-bed analytical set-up for the further investigation into pellet combustion in this reactor.

The size and shape of the pellets were modified, due to the difficulties experienced feeding with the system available. The new pellets, shown schematically in Figure 9.2, were 15.5 mm x 12.5 mm and each weighed approximately 1.8 g. These pellets had a bulk density of 496 kg/m^3 after drying. To form these pellets, the two materials were dried to ~10 % moisture and then thoroughly mixed in a 50:50 wt% ratio, prior to pelletisation in a compression pelletiser. After formation, they were dried further, until the moisture content was in equilibrium with the laboratory (~ 2-4 %) to ensure a high CV and maximise the potential for energy recovery.

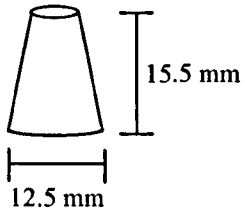


Figure 9.2 SMC-coal tailing pellet used for the in-depth fluidised-bed combustion tests.

9.2.2 Experimental Conditions

Twelve combustion cases were devised, with the aim of exploring the effects of manipulating three key variables: (i) the pellet feedrate, (ii) the primary (fluidising and combustion) air flowrate and (iii) the depth of the sand bed. The experimental conditions for these cases are shown in Table 9.1. The variation of the first two parameters altered the air-to-fuel ratio (air ratio) within the combustor; this was calculated based on the combustion conditions, namely the total amounts of air and fuel, and the fuel characteristics, specifically the oxygen required to completely burn all carbon (41.6 %), hydrogen (3.2 %) and sulphur (2.1 %) present in the fuel pellets. Each kg of SMC-coal tailing fuel pellets required 5.45 kg of air for stoichiometric combustion conditions to prevail in the combustor. All cases used excess air – fuel-lean conditions; combustion was not attempted with sub-stoichiometric air, as efficiency would be too low, encouraging the formation of unwanted pollutant species, such as unburned hydrocarbons and CO due to incomplete combustion. Based on the results of the material characterisation in Chapter 6, the air ratio for each case was calculated, shown in the table below. A range of values were examined, where excess air ranged from 61 % (Case 6) to 276 % (Case 2).

CASE	PRIMARY AIR (kg/m^2hr)	PELLET FEEDRATE (kg/hr)	AIR RATIO	EXCESS AIR (%)	DEPTH OF SAND BED (m)
1	415	3.52	2.13	113	0.22
2	415	2.02	3.76	276	0.22
3	415	2.46	3.08	208	0.22
4	415	2.99	2.54	154	0.22
5	415	4.05	1.87	87	0.22
6	415	4.58	1.61	61	0.22
7	277	3.52	1.65	65	0.22
8	330	3.52	1.84	84	0.22
9	468	3.52	2.35	135	0.22
10	511	3.52	2.51	151	0.22
11	606	3.52	3.02	202	0.22
12	415	3.52	2.13	113	0.27

Table 9.1: The test variables that were manipulated for the twelve cases in the fluidised-bed.

The first case was the reference, to which all other tests were compared; this had a moderate primary air flowrate and a moderate pellet feedrate. Cases 2 to 6 assessed the impacts of altering the first variable, the pellet feedrate; a range of values greater and lower than that used in the reference case were compared, ranging from 2.02 kg/hr to 4.58 kg/hr (115-260 kg/m^2hr). The small SMC-coal tailing pellets were fed with an auger screw, which was calibrated at varying feedrates (Figure 9.3). Cases 7 to 11 investigated the effect of changing the primary air flowrate, by increasing and decreasing the air to the

system from the reference case. The air flowrates tested ranged from 277 kg/m^{2}hr to 606 kg/m^{2}hr (4.9-10.7 kg/hr). Secondary air was kept almost constant for comparison. Lastly, Case 12 looked at the effect of altering the sand bed depth. Due to difficulties involved with attempting to fluidise the bed during the preliminary investigations, lower bed depths (0.22 m and 0.27 m instead of 0.30 m) were used to ensure proper fluidisation and limit slugging. The bed depth could not be increased too far as there were issues with gaining fluidisation to a satisfactory level and thus unfortunately a range of bed depths could not be practically investigated, hence why only two values were compared for this variable.

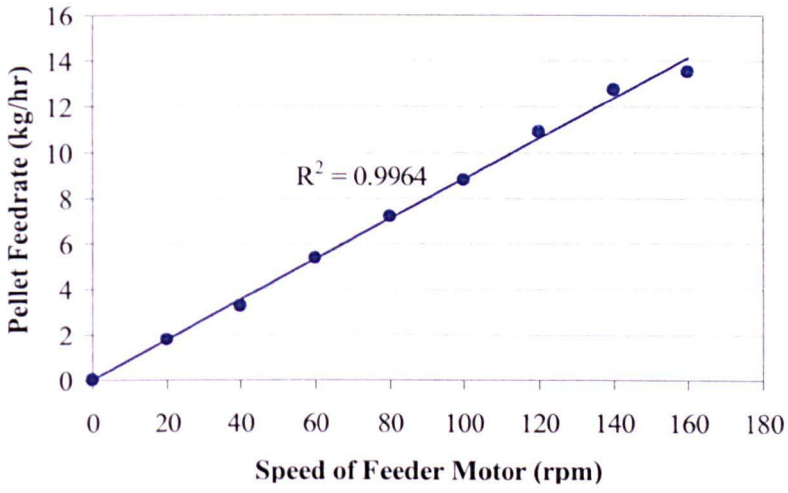


Figure 9.3: Calibration of the motor speed and pellet feedrate, fed with the auger screw.

9.2.3 Data Analysis

The effect of manipulating these three variables was assessed; these included impacts on the temperature profiles, various gas concentrations and the properties and composition of the flyash.

9.2.3.1 Temperatures

The temperatures were monitored and logged at eight locations throughout the bed and freeboard, as described for the preliminary investigation in Section 8.5.1 and Table 8.4. The results focussed on three thermocouples: T2, within the sand bed; T4, just above the sand bed; and T7, towards the top of the freeboard. In addition, the temperature increase in °C/min was calculated for each case from these data for the duration of the combustion phase, also for the three main thermocouples (T2, T3 and T7).

9.2.3.2 Gaseous Emissions

The flue gas concentrations (O_2, CO_2 and CO) were measured using an ADC MGA3000 gas analyser, as outlined in Section 8.5.1. From the averaged data, the combustion efficiency (η_{CE}) was calculated for each case, using Equation 8.1. Heat loss due to incomplete combustion (due to the formation of CO instead of CO_2) was also computed, as the actual heat loss, in MJ/kg of fuel, and then as a percentage of the total heat input. This was based on fuel composition, fuel NCV, the exhaust composition and the enthalpies of the relevant combustion reactions (Table 9.2), namely those outlined in Equation 3.2.

COMBUSTION REACTION	ENTHALPY OF COMBUSTION (ΔH in MJ/kg)
$C + O_2 \rightarrow CO_2$	33.96
$C + \frac{1}{2}O_2 \rightarrow CO$	10.23
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	133.50

Table 9.2: The enthalpies of the combustion reactions outlined in Equation 3.2.

The combustion of these pellets on an industrial scale for the purpose of energy recovery must comply with the Waste Incineration Directive, outlined in Section 2.3.3 and Table 2.6, which limits NOx, SO_2 and HCl emissions, among others. Consequently, NOx were measured using a Signal Series 4000 NOx analyser and the gas was also analysed for other acid gas species (sulphates and chlorides), using the wet chemical method followed by gas ion chromatography; further details were given in Section 8.5.1. Whilst Ca is thought to be useful in reducing SOx emissions, the presence of phosphorous can interfere with the capture mechanism; thus the amounts of Ca and P in the initial material and the ash were compared and related to the amounts of sulphates in the exhaust gases (Altun, *et al.*, 2006; Elled, *et al.*, 2006).

Additionally, four sampling ports (P1-P4), identified in Table 9.3, were used for taking gas samples at the wall of the reactor. These were then analysed with a Varian CP 3800 gas chromatograph/gas chromatograph mass spectrometer, also described in Section 8.5.1, for short-chain hydrocarbons, volatile organic compounds and hydrogen. This was to investigate fuel gas formation and burnout.

SAMPLING PORT	P1	P2	P3	P4
Height Above Plate (m)	0.11	0.20	0.56	cyclone exit

Table 9.3: Locations of the four gas sampling ports in the fluidised-bed.

9.2.3.3 Ash Analysis

The gases produced passed through a 0.1 m diameter and 0.4 m high stainless steel cyclone at the combustor exit to remove inorganic particulate matter (flyash) before being analysed or discharged to the atmosphere. The particulates collected in the cyclone were subsequently weighed and analysed. These included elemental analysis, a determination of the proportion of C, H, N, Cl and unburned carbon in each sample and various factors to assess the slagging and fouling behaviour of the ash.

Firstly, the particulates underwent elemental analysis, using the acid digestion method described in Section 8.5.1. This gave the composition of the ash, focusing specifically on the metal contaminants, in particular the alkali, transition and heavy metal content. This test was repeated for each flyash sample. The results were compared to the initial feed material, which was vital as the concentrations of specific elements in the initial fuel do not necessarily correspond to those found in the ash (Kouvo and Backman, 2003). Their release is reliant on a complex process, the factors of which were outlined in Section 4.5.3. Secondly, the remaining combustible material (unburned carbon) was experimentally-determined, to assess the validity of the combustion efficiencies calculated using the exhaust gas concentrations. This

was measured by placing two 1 g samples of the ash into a furnace (at 750 °C) for one hour. Thirdly, C, H, N and Cl were determined using ultimate analyses testing of the ash samples, as described in Section 6.2.2; this forms part of the British Standard 1016, Part 6: 1977 (British Standards Institution, 1977a).

Lastly, the slagging and fouling behaviour of the flyash was investigated in a variety of ways. The Alkali Index (AI) was calculated for each case using the elemental composition of the flyash as input data for Eq. 8.9. Another measure of problematic deposition occurring is the presence of silicon, aluminium and iron in oxide form in the ash, the concentrations of which were also determined in the elemental analysis. A correlation between the amounts of these present and slag/deposit formation has been found, where Si appears to be the most influential (Öhman, *et al.*, 2004). Fryda, *et al.* (2006) found that the presence of potassium, silicon, chlorine and phosphorus could also lead to ash agglomeration, as considered in Section 4.5.2, thus the concentrations of these in the ash were also examined. Jenkins, et al. (1998) also commented that Si, Cl and S in the ash can contribute to the formation of detrimental compounds.

The fusion temperatures were also determined for flyash samples by heating a small cone of the ash in a reducing atmosphere (50 % hydrogen and 50 % carbon dioxide) until it started to melt, according to British Standard 1016, Part 15: 1970 (British Standards Institution, 1970). Temperatures were determined for (i) initial deformation, where the edges of the tip of the mound became rounded; (ii) the hemispherical stage, where the entire cone became hemispherical, such that the height (h_h) was equal to half the base (b) ($h_h = ½b$); and lastly (iii) the fluid/flow stage, where the ash melted and became flat, such that the height (h_f) was equal to a third of that at the hemispherical stage ($h_f = ⅓h_h$). This can also indicate slagging and fouling, although accuracy can be problematic as the results often have a high percentage error (British Standards Institution, 1970). This was repeated twice for each flyash sample.

9.3 RESULTS AND ANALYSIS OF MANIPULATING THE COMBUSTION VARIABLES

The experiments were performed to assess alterations of the key variables; these results are presented and analysed here. The effect of changing these variables can be clearly seen in all cases, on the air ratios, temperatures and gas concentrations (and consequently, also on the overall combustion efficiency). The tests were repeated to ensure the accuracy and validity of the results; the complete data set is given in Table 9.4, with averaged results given separately in each section below. Due to the number of tests performed for each case, 95 % Confidence Limits are shown as error bars on the graphs to illustrate the variation in the data. Due to the lower bed depths used than for the preliminary tests described in Chapter 8, proper fluidisation was seen for all experiments. Despite the variations in air flowrates between the cases, the pressure drop of the system, ΔP, calculated using Equation 4.2, was 3.44 kPa for all cases where the bed depth was 0.22 m. Where a deeper bed was employed (0.27 m), the pressure drop increased to 4.05 kPa. Armesto, *et al.* (2003) used 40 kPa for their bubbling fluidised-bed, whereas Elled, *et al.* (2006) used a ΔP of 6.5 kPa in a circulating fluidised-bed.

PARAMETER		CASE																			
		1			2	3		4		5		6	7		8		9	10	11	12	
Run		1	2	3	1	1	2	1	2	1	2	1	1	2	1	2	1	1	1	1	2
Pellet Feedrate (kg/hr)		3.52	3.52	3.52	2.02	2.46	2.46	2.99	2.99	4.05	4.05	4.58	3.52	3.52	3.52	3.52	3.52	3.52	3.52	3.52	3.52
Primary Air (kg/m^{2}hr)		415	415	415	415	415	415	415	415	415	415	415	277	277	330	330	468	511	606	415	415
Secondary Air (kg/m^{2}hr)		155	170	170	170	170	170	170	170	170	170	155	170	170	170	170	170	170	213	170	170
Depth of Sand Bed (m)		0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.27	0.27
Bed Depth-to-Diameter Ratio		1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.80	1.80
Air Ratio		2.10	2.16	2.16	3.76	3.08	3.08	2.54	2.54	1.87	1.87	1.61	1.65	1.65	1.84	1.84	2.35	2.51	3.02	2.16	2.16
Average Gas Concentration	CO_2 (%)	12.47	15.29	15.88	4.87	13.40	15.28	15.24	12.99	15.25	16.19	16.39	14.59	17.23	16.95	16.82	16.13	14.90	13.98	15.40	15.67
	O_2 (%)	6.22	3.46	2.17	15.37	5.55	4.10	3.20	6.01	2.91	1.98	1.82	3.46	1.00	0.78	0.93	2.89	3.62	4.47	2.06	2.39
	CO (%)	0.61	0.53	1.18	0.10	0.38	0.48	0.80	0.43	0.90	0.91	2.47	1.82	1.88	1.94	1.82	0.85	0.83	0.52	1.11	2.03
	NOx (ppm)	16.09	8.03	45.5	2.09	13.25	23.13	14.63	5.25	7.75	-	4.34	3.98	58.38	10.42	7.65	2.40	-	37.88	32.38	36.43
Heat Loss Due to Incomplete Combustion	MJ/kg fuel	0.46	0.33	0.68	0.20	0.27	0.30	0.49	0.32	0.55	0.52	1.29	1.09	0.97	1.01	0.96	0.49	0.52	0.35	0.66	1.13
	% Heat Input	2.85	2.05	4.23	1.23	1.69	1.86	3.05	1.96	3.41	3.26	8.02	6.79	6.02	6.29	5.98	3.06	3.23	2.20	4.12	7.02
Combustion Efficiency (%)		95.34	96.65	93.08	97.98	97.24	96.95	95.01	96.80	94.43	94.68	86.93	88.91	90.16	89.73	90.24	94.99	94.71	96.41	93.28	88.53
Average Temperature (°C)	Bed	865	876	865	848	825	843	866	860	894	863	887	839	874	865	835	879	862	842	870	865
	Above Bed	863	876	866	825	825	847	869	861	897	865	892	792	861	854	828	881	861	843	868	866
	Freeboard	531	533	450	423	433	484	541	494	567	536	577	387	484	485	414	525	476	502	441	486
Temperature Increase (°C/min)	Bed	2.63	2.95	2.34	1.26	1.33	2.02	3.23	3.19	3.44	3.50	3.74	1.69	2.87	2.49	1.75	2.56	3.29	3.38	1.68	2.32
	Above Bed	3.14	3.18	2.37	2.17	1.62	1.98	3.48	3.29	3.62	3.47	3.57	1.90	1.92	2.59	1.93	2.57	3.74	3.67	1.94	2.45
	Freeboard	1.37	1.73	2.66	0.98	2.17	0.78	1.23	2.52	1.72	2.06	1.55	2.90	0.66	1.29	1.85	1.65	2.77	3.19	0.60	1.82

Table 9.4: Table showing the operating conditions for the twelve cases and results for gas concentrations, combustion efficiency, temperatures and temperature increases for pellet combustion in the fluidised-bed. Case 1 is the base test, Cases 2 to 6 are those which alter the pellet feedrate, Cases 7 through 11 are those which alter the primary/fluidising air flowrate and Case 12 is where the depth of the sand bed was increased.

9.3.1 Effect of Changing the Pellet Feedrate

The reference case (Case 1) and first set of cases (Cases 2-6) concerned the effect of altering the pellet feedrate and thus these looked at the air ratio and combustion stoichiometry. The pellet feedrate varied from 2.02 kg/hr to 4.58 kg/hr while other variables remained constant, achieving air ratios of 1.61-3.76 (61-276 % excess air). Combustion was not attempted with sub-stoichiometric air. The conditions for these experiments are shown in Table 9.5 along with the mean results of the gas concentrations, heat loss, combustion efficiency and temperatures for each case; more details of individual tests were given in Table 9.4. The impact of changing the pellet feedrate had obvious implications on the gas concentrations, η_{CE} and temperatures, as shown on Figures 9.4 and 9.5.

PARAMETER		CASE 1	CASE 2	CASE 3	CASE 4	CASE 5	CASE 6
Pellet Feedrate (kg/hr)		3.52	2.02	2.46	2.99	4.05	4.58
Primary Air (kg/m^{2}hr)		415	415	415	415	415	415
Secondary Air (kg/m^{2}hr)		165	170	170	170	170	163
Depth of Sand Bed (m)		0.22	0.22	0.22	0.22	0.22	0.22
Air Ratio		2.14	3.76	3.08	2.54	1.87	1.61
Average Gas Concentration	CO_2 (%)	14.55	4.87	14.34	14.12	15.72	16.39
	O_2 (%)	3.95	15.37	4.83	4.61	2.45	1.82
	CO (%)	0.77	0.10	0.43	0.62	0.91	2.47
	NOx (ppm)	23.21	2.09	18.19	9.94	7.75	4.34
Heat Loss Due to Incomplete Combustion	MJ/kg fuel	0.51	0.20	0.27	0.40	0.53	1.30
	% of Heat Input	3.18	1.22	1.67	2.50	3.32	8.10
Combustion Efficiency, η_{CE} (%)		95.02	97.98	97.10	95.90	94.55	86.93
Average Temperature (°C)	Bed	869	848	834	863	879	887
	Above Bed	868	825	836	865	881	892
	Freeboard	505	423	459	518	552	577
Temperature Increase (°C/min)	Bed	2.64	1.26	1.68	3.21	3.47	3.74
	Above Bed	2.89	2.17	1.80	3.38	3.54	3.57
	Freeboard	1.92	0.98	1.47	1.87	1.89	1.55

Table 9.5: Combustion conditions and average results from the test cases assessing the effects of manipulating the pellet feedrate.

As expected and seen on Figure 9.4, when the pellet feedrate increased (i.e. the air ratio decreased), the O_2 concentration was reduced and consequently CO_2 increased; these correlations were quite strong and significant, shown by the coefficients of determination. There was more incomplete combustion due to the insufficient air provided, and consequently CO increased. The η_{CE} is based on the concentrations of CO and CO_2 and there was also a strong correlation between pellet feedrate and η_{CE}. Heat loss due to incomplete combustion closely mirrored the CO concentration and therefore had the opposite relationship with η_{CE}. As the pellet feedrate increased, there was a greater abundance of fuel with diminishing amounts of air, thus η_{CE} decreased rapidly once the air ratio fell below 1.8, corresponding to feedrates above 4 kg/hr. NOx were also monitored; the concentration varied (2.09-23.21 ppm), but was low.

The temperatures and rates of temperature increase were also significantly influenced by the alterations in the pellet feedrate (Figures 9.5 and 9.6). The temperatures within the sand bed (T2, y=0.20 m) and just above it (T4, y=0.42 m) were high, well in excess of 800 °C in all cases; these increased slightly with

each case so the overall temperature increase was around 60 °C between the slowest and fastest feedrates (largest and smallest air ratios). The effect that increasing the pellet feedrate had higher up in the reactor, in the freeboard, were far more pronounced, where the temperature near the top of the freeboard (T7, y=1.54 m) increased dramatically. The temperature difference exceeded 150 °C between the fastest and slowest feedrates. These correlations were very significant, especially for T4 and T7.

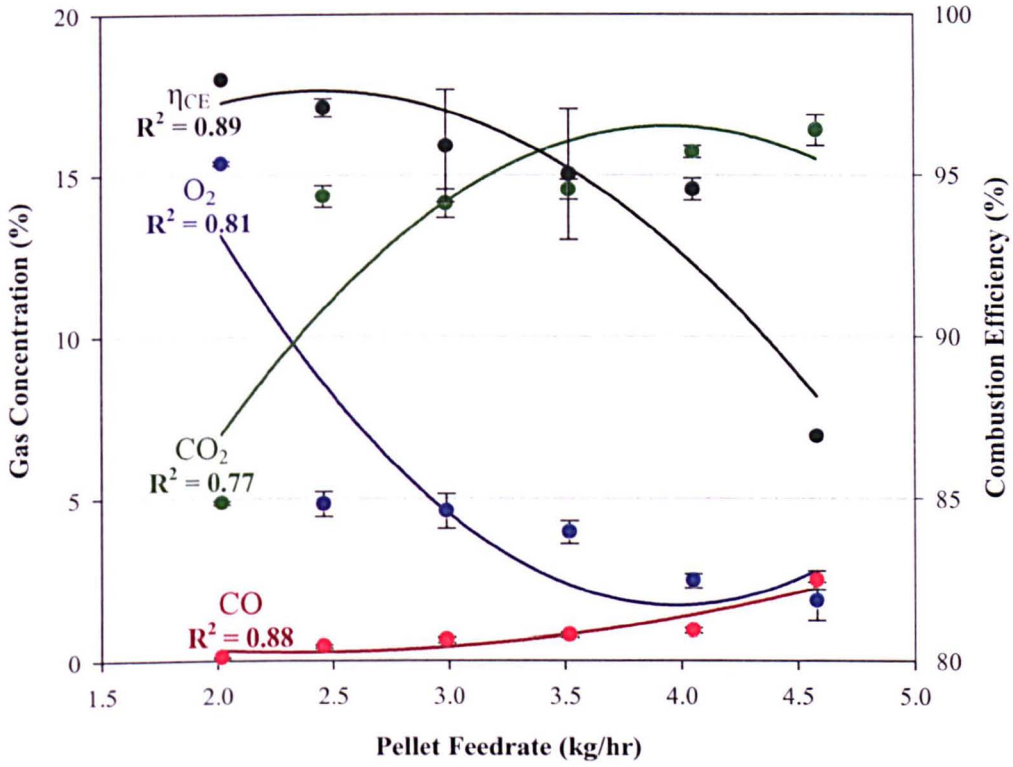


Figure 9.4: Trends for the exhaust gas concentrations and efficiency with increasing pellet feedrates.

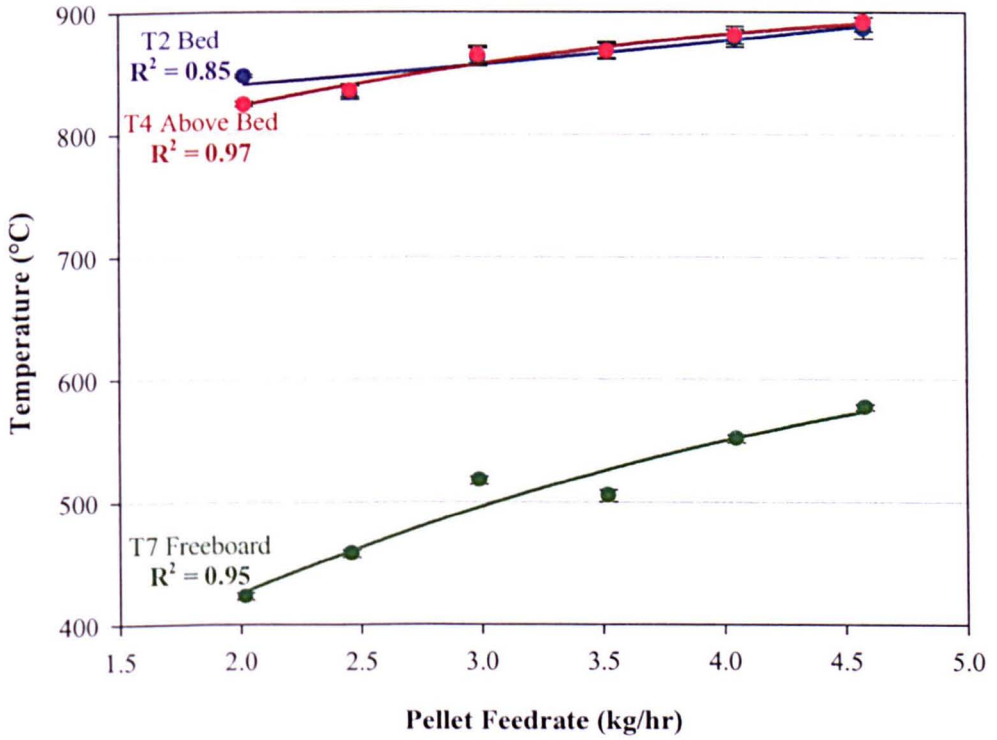


Figure 9.5: Trends for the temperatures throughout the reactor with increasing pellet feedrates.

As shown in Table 9.5 and Figure 9.6, the heating rate was also appreciably affected by the pellet feedrate. As the feedrate became faster, the rate of temperature increase also became more rapid in and just above the bed (T2 and T4); these were both quite significant correlations and were fairly similar. The relationship between T7, in the freeboard, and the pellet feedrate, however, was somewhat dissimilar, although more significant than those for T2 and T4. Here, the rate of temperature increase became more rapid as the feedrate became faster, until the pellet feedrate reached 3.5 kg/hr; above this, the rate of temperature change decreased. It is also worth noting that the rate of temperature increase was significantly lower in the freeboard compared to those in and above the bed.

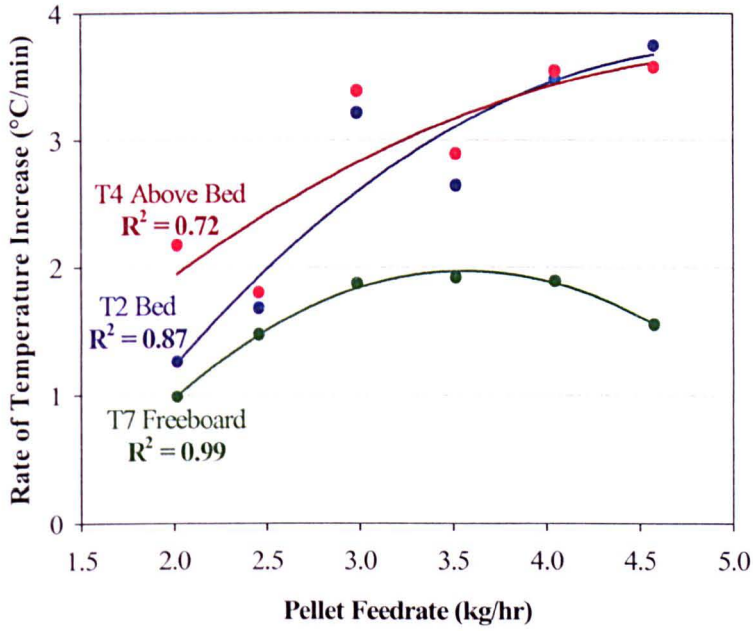


Figure 9.6: Trends for the initial rate of temperature increase with increasing pellet feedrates.

9.3.2 Effect of Changing the Primary/Fluidising Air Flowrate

The second set of tests, Cases 7-11 investigated the impacts of changing the primary (fluidising) air flowrate and thus the air ratio and stoichiometry of combustion. Other variables remained constant, while the primary air varied from 277 kg/m^{2}hr to 606 kg/m^{2}hr, achieving air ratios of 1.65-3.02 (65-202 % excess air), similar to the above cases. Again, combustion was not attempted with sub-stoichiometric air. The combustion conditions and results can be compared for these tests in Table 9.6, which shows the average values. A more in-depth overview of individual tests for each case was given in Table 9.4.

Altering the primary air had as significant an effect on the temperatures as the variation of the pellet feedrate; its impacts however were less apparent on the gas concentrations, even though these were clear for the above cases. The correlation between the primary air and the O_2 concentration appeared not to be as strong as that for the pellet feedrate; the same was also true for CO_2 (Figure 9.7). Whilst there were some trends indicated in both cases, these were not as clear as expected with the increasing air ratios. The CO correlation was much more significant and there was a clear relationship between this and the primary air flowrate; as expected, the incomplete combustion reactions – which produce CO – became less

abundant as the air ratio increased due to greater primary air flows. The η_{CE}, which was dependent on the CO and CO_2 concentrations, however did follow a distinct trend, improving considerably with increasing primary air flowrates. Heat loss due to incomplete combustion showed the same trends as the above tests. Again, NOx emissions varied, but were low and similar to those recorded above.

PARAMETER		CASE 1	CASE 7	CASE 8	CASE 9	CASE 10	CASE 11
Pellet Feedrate (kg/hr)		3.52	3.52	3.52	3.52	3.52	3.52
Primary Air (kg/m^{2}hr)		415	277	330	468	511	606
Secondary Air (kg/m^{2}hr)		163	170	170	170	170	213
Depth of Sand Bed (m)		0.22	0.22	0.22	0.22	0.22	0.22
Air Ratio		2.14	1.65	1.84	2.35	2.51	3.02
Average Gas Concentration	CO_2 (%)	14.55	15.91	16.89	16.13	14.90	13.98
	O_2 (%)	3.95	2.23	0.86	2.89	3.62	4.47
	CO (%)	0.77	1.85	1.88	0.85	0.83	0.52
	NOx (ppm)	23.21	31.18	9.04	2.40	-	37.88
Heat Loss Due to Incomplete Combustion	MJ/kg fuel	0.51	1.05	1.00	0.52	0.50	0.34
	% of Heat Input	3.18	6.53	6.19	3.24	3.12	2.11
Combustion Efficiency, η_{CE} (%)		95.02	89.54	89.98	94.99	94.71	96.41
Average Temperature (°C)	Bed	869	857	850	879	862	842
	Above Bed	868	827	841	881	861	843
	Freeboard	505	436	450	525	476	502
Temperature Increase (°C/min)	Bed	2.64	2.28	2.12	2.56	3.29	3.38
	Above Bed	2.89	1.91	2.26	2.57	3.74	3.67
	Freeboard	1.92	1.78	1.57	1.65	2.77	3.19

Table 9.6: Average results from the tests carried out to assess the effects of manipulating the primary (fluidising) air flowrate.

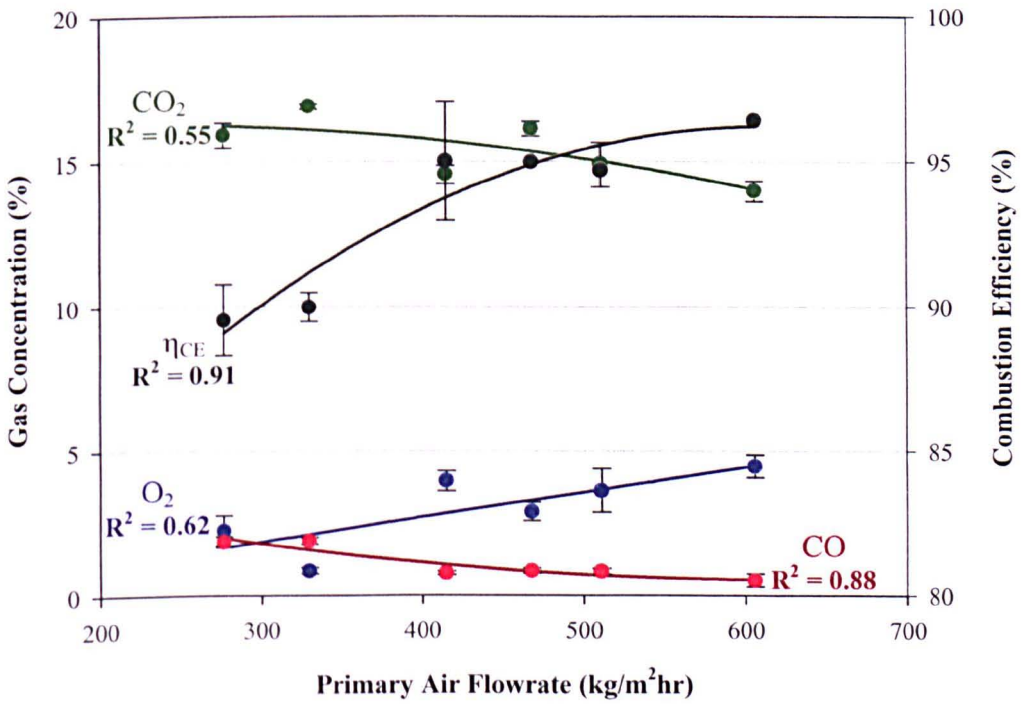


Figure 9.7: Trends for the gas concentrations and combustion efficiency with increasing primary air.

As stated above, altering the primary air flowrate had significant implications on the temperatures in both the bed and the freeboard; this is shown clearly for the three main thermocouples in Figure 9.8, but the trends were distinctly different than those expressed in Figure 9.5 for the fuel feedrate, which were fairly

linear. Here, the temperature increased as the air ratio increased, up to air flowrates of approximately 450-475 kg/m^{2}hr (air ratios of 2.33-2.43); after this, the excess air in the system became too great and cooled the reactions. As with the pellet feedrate cases, the thermocouples located within and just above the bed (T2 and T4) had the highest temperatures, with those in the top of the freeboard (T7) being significantly lower. The temperatures recorded for these and the above cases were, however, comparable. The correlations for the rates of temperature increase were significant (Figure 9.9), where the freeboard had the slowest temperature rise and just above the bed generally had the fastest, as with the pellet feedrate.

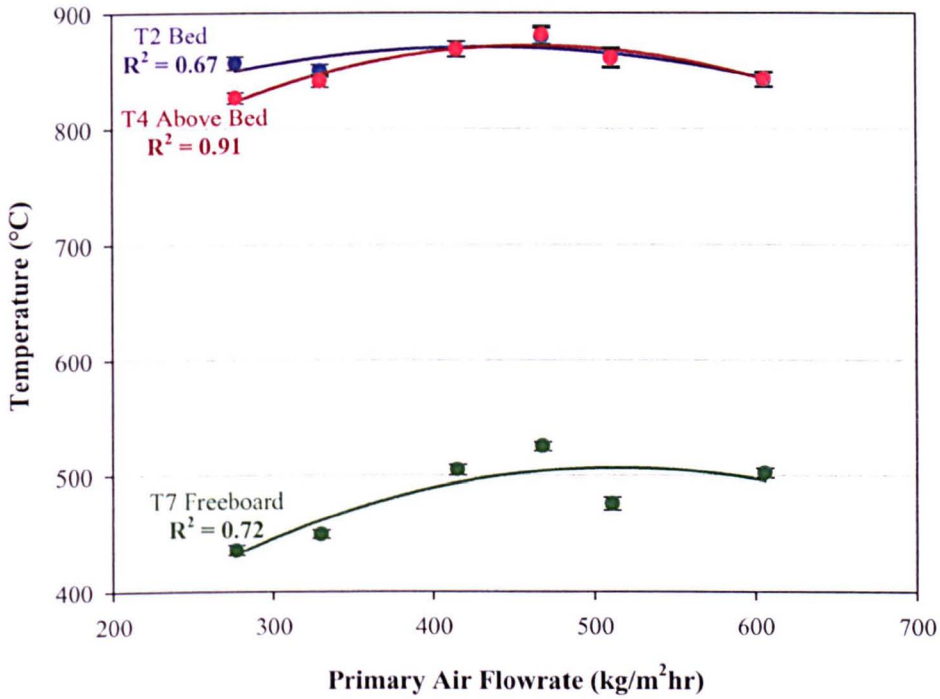


Figure 9.8: Trends for the temperatures throughout the reactor with increasing primary air flowrates.

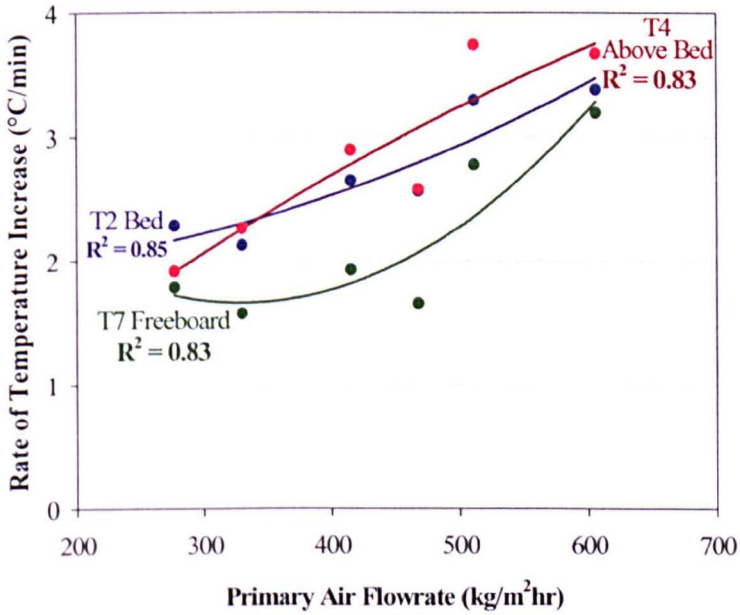


Figure 9.9: Trends for the rate of initial temperature increase with increasing primary air flowrates.

9.3.3 Effect of Changing the Depth of the Sand Bed

The final case (12) investigated the impacts of the increasing bed depth; the stoichiometry was the same as Case 1. As only two bed depths were investigated, due to the constraints detailed above, it was difficult to form meaningful correlations between the results. Averaged results are shown in Table 9.7 below and the data of all the tests were presented in Table 9.4.

PARAMETER		CASE 1	CASE 12
Pellet Feedrate (kg/hr)		3.52	3.52
Primary Air (kg/m^{2}hr)		415	415
Secondary Air (kg/m^{2}hr)		163	170
Depth of Sand Bed (m)		0.22	0.27
Air Ratio		2.14	2.16
Average Gas Concentration	CO_2 (%)	14.55	15.54
	O_2 (%)	3.95	2.23
	CO (%)	0.77	1.57
	NOx (ppm)	23.21	34.41
Heat Loss Due to Incomplete Combustion	MJ/kg fuel	0.51	0.92
	% of Heat Input	3.18	5.73
Combustion Efficiency, η_{CE} (%)		95.02	90.90
Average Temperature (°C)	Bed	869	868
	Above Bed	868	867
	Freeboard	505	464
Temperature Increase (°C/min)	Bed	2.64	2.00
	Above Bed	2.89	2.19
	Freeboard	1.92	1.21

Table 9.7: Average results from the tests to assess the effects of altering the depth of the sand bed.

There was some noticeable variation in the data for the different bed depths. The gas concentrations indicated more incomplete combustion occurred for the deeper bed, as the CO concentration was higher. The η_{CE} was thus severely reduced from 95.0 % to 90.9 %. NOx concentrations were also greater. Although there were large differences in the freeboard temperatures – just over 40 °C with the deeper bed resulting in a cooler freeboard, those in the bed were the same. The rates of temperature increase were different but followed the same pattern, with freeboard temperatures rising more slowly. A deeper bed with more sand to heat resulted in slower heating rates.

9.3.4 Fuel Gas Formation and Burnout

Gas samples were taken from four sampling ports during combustion and were analysed for short-chain hydrocarbons, volatile organic compounds and hydrogen using a Varian CP 3800 gas chromatograph/gas chromatograph mass spectrometer. Sampling ports P1 and P2 were located in the sand bed, y=0.11 m and y=0.20 m respectively, and P3 was located above the bed, below the entrance of the fuel and secondary air (y=0.56 m); no fuel gases were found in any samples, as they were taken from the walls of the combustor where the air collects, not from the centre where reactions occur. Due to the design constraints, these are not suitable sampling locations. No hydrocarbons were present in the freeboard (P4, cyclone exit), although 0.015 % of hydrogen was found.

9.3.5 Acid Gas Emissions

Various techniques were used to monitor the concentrations of NOx, SOx and HCl emissions during each test; the comparison of these to WID emission limits is considered in the subsequent chapter. The results for NOx were shown in Tables 9.4-9.7. NO and NO_2 concentrations ranged from 2.1-58.4 ppm, which were low; this was predicted by previous literature, which reports that SMC combusted in a fluidised-bed will produce minimal NOx due to the oxidation of fuel nitrogen (Williams, 2001; Williams, *et al.*, 2001a; Chugh and Patwardhan, 2004). Accordingly, the NOx formed were most likely from a thermal source, as much nitrogen was contained in the combustion air; this would account for the emissions detected here. Consequently, it was thought that the majority of nitrogen in the fuel (1.76 %) would remain in the ash as nitrates, although some was captured in the hydrogen peroxide solution (Table 9.8). The nitrogen content of the ash, however, was not as high as expected (0.29 %, as considered below), thus the nitrogen was probably released as N_2O gas, though measurement of this species was beyond the scope of this project. While this is not an acid gas and consequently not classed as a NOx compound, it is a greenhouse gas and therefore its formation is undesirable. Unfortunately, fluidised-bed combustors are particularly prone to N_2O formation, as considered above, even though NOx are usually low, as seen here.

SO_4^{2-} and Cl^- species were captured from the flue gases during combustion to indicate the presence of SOx and HCl. The results of this analysis are presented in Table 9.8. The amount of sulphates present was low (2.35-41.69 ppm), indicating that the SOx concentration was also likely to be minimal. As the Ca content of the fuel was significant (29,680 mg/kg), due to the lime in the SMC casing, this may have aided the reduction of SOx, as this is used in lime scrubbing (Altun, *et al.*, 2006). There was 3121 mg/kg of P also in the initial fuel, which may have impeded the effect of Ca in minimising the SOx emissions. The S was found to be concentrated in the ash (15,000 mg/kg), considered further below (Table 9.9).

SPECIES	AVERAGE CONCENTRATION (ppm)	95 % CONFIDENCE
Fluoride	0.44	0.36
Chloride	5.33	3.12
Nitrite	0.30	0.08
Nitrate	3.78	0.43
Phosphate	3.90	1.62
Sulphate	12.03	7.81
Sodium	3.05	0.81
Ammonium	3.53	2.81
Potassium	0.61	0.38
Calcium	2.79	1.64

Table 9.8: Average concentration and standard deviation for pollutant species produced during the fluidised-bed combustion of SMC-coal tailing pellets.

The chlorides present ranged from 0.88 ppm to 16.88 ppm, which is also minimal. As with the sulphur, the Cl was concentrated in the ash (535 mg/kg). This may however contribute to ash agglomeration (Jenkins, *et al.*, 1998; Fryda, *et al.*, 2006). In addition to the sulphates and chlorides, which were by far the most dominant species present, the tests also indicated the presence of other compounds, as well as

metals (Table 9.8). Of these, phosphates, ammonium, nitrates and sodium were the most abundant, but their concentrations were still low. Furthermore, a number of unidentified peaks were present on the chromatograph, predominantly anions although a few cation species were also detected.

9.3.6 Flyash Analysis: Properties and Composition

Flyash was collected from the cyclone after each test for further analysis. A large proportion of the ash in the initial fuel remained as fine ash, on average 80 % after combustion. The rest, along with any that formed on combustion, was either emitted with the flue gases if the particles were too small to be collected by the cyclone or remained in the bed if the particles were large and unable to elutriate; it is likely that the first of these is most probable, as there were minimal traces of ash in the bed on inspection.

The elemental analysis of the ash samples looked specifically for metal contaminants, in particular, Na and K to compute the Alkali Index, along with S, Si, Al, Fe and P, which can also cause issues. Nine test runs were carried out; Table 9.9 indicates the cases which were assessed for each, as well as the elemental analysis and AI. The metals found in the largest amounts were Al, Ca, Fe, Mg, Na and K. Other elements, such as S, P and Si were also found in large quantities. Slagging and fouling were also investigated, by firstly computing the AI from the amounts of Na and K. As the values are towards the lower end of the 0.17-0.34 kg-alkali/GJ range, fouling is probable, but not certain. The amounts of Si, Al and Fe were also ascertained, as high proportions of these in oxide form can lead to slagging within the system (Öhman, *et al.*, 2004). Whilst Al and Fe were quite profuse (45,000 mg/kg and 37,250 mg/kg respectively), Si, which is thought to be more influential, was not so abundant. Critical levels of SiO_2 in the ash are thought to be in the region of 20-25 wt%, although the amounts noted here were significantly below this in all cases, even though the Si appears to be concentrated in the flyash (Öhman, *et al.*, 2004). It was previously considered that in addition to K and Si, already taken into account, Cl, S and P may also aid ash agglomeration (Fryda, *et al.*, 2006). The Cl and S present in the initial fuel have already been found to be concentrated in the ash. This also appears to be the case for P, seen in Table 9.9, thus the presence of several elements known to cause slagging, fouling and agglomeration have been identified in the ash. The low temperatures in the fluidised-bed however appeared to limit slag formation.

C, H, N, S and Cl concentrations were also determined for each test (Table 9.10). Although the nitrogen and thus the nitrate concentration in the ash was low, as considered above, the S and Cl content were significantly higher, and thus sulphates and chlorides, the SOx and HCl forming species, remained in the flyash, leading to the low emissions contemplated above. There were also high proportions of C in the ash and, on average, 13 % combustible material. This strongly suggests that the combustion efficiencies based on the CO and CO_2 concentrations may not be as high as indicated. Although inefficiencies in the combustor are a likely source of this unburned material, fuel particle carryover, particularly dust formed during pellet feeding, would have also significantly contributed to this, as light SMC particles could have been elutriated by the high air flowrates rather than being burned in the bed.

COMPONENT (mg/kg)	PELLETS	AVERAGE	ASH FROM RUN							
			A	B	C	D	E	F	G	H
Test Cases	-	-	1, 2, 6	7, 1	10	4, 5, 8, 11	3, 4, 5	8, 9	1, 3, 7	12, 12
Flyash as % of Ash in Pellets	-	78.95	65.72	92.08	87.37	74.23	70.22	83.74	84.05	69.22
Alkali Index (kg-alkali/GJ)	-	0.235	0.239	0.225	0.368	0.220	0.226	0.243	0.248	0.243
Al	2500	45000	46000	43000	45000	44000	44000	48000	45000	45000
As	8	51	62	50	49	54	51	40	50	52
B	14	47.6	50	44	44	45	44	52	49	53
Ba	149	683.8	690	660	680	690	690	730	680	650
Ca	29680	68375	67000	69000	67000	60000	65000	71000	75000	73000
Cd	0	4.0	5.0	3.0	7.0	4.3	3.9	2.8	2.8	3.0
Ce	3	62	62	62	59	64	64	64	59	62
Co	5	17.4	17	17	17	18	17	18	17	18
Cr	9	52.5	64	46	48	60	52	52	51	47
Cu	29	126.3	130	120	140	120	120	130	130	120
Fe	5604	37250	40000	35000	35000	41000	39000	36000	37000	35000
Ga	-	12.4	13	12	13	13	13	12	12	11
K	8364	20625	21000	19000	21000	18000	19000	22000	23000	22000
La	1	31.9	34	32	31	34	33	30	31	30
Li	6	40.1	33	42	42	40	43	45	43	33
Mg	3485	8325	8000	8600	8200	7700	7900	8900	8800	8500
Mn	196	513.8	580	510	470	550	550	510	480	460
Mo	3	10	10	9.2	11	11	9.8	9.4	9.8	10
Na	1123	3750	4000	3700	3900	3600	3700	3700	3800	3600
Nd	-	26.6	26	26	26	27	27	27	26	28
Ni	13	58.8	65	62	67	66	55	50	56	47
P	3121	5237.5	7100	5100	4200	5600	5600	4800	4800	4700
Pb	8	45	64	41	42	51	50	40	36	36
S	11702	15300	13600	16100	14600	14300	14500	15300	16900	17100
Sc	1	8.7	8.6	8.3	8.6	8.2	8.5	9.5	9.1	9.1
Si	1487	3137.5	3100	2800	3300	3400	3300	2900	3300	3000
Sr	105	281.9	300	275	275	255	265	280	300	305
Ti	22	502.5	520	390	500	500	480	500	610	520
V	7	78.5	85	72	74	70	73	85	81	88
Y	2	7.9	8.1	7.5	7.8	7.9	7.8	7.9	7.8	8.2
Zn	100	198.8	270	160	210	220	190	180	190	170
Zr	1	8.9	7.4	8.4	9.1	9.2	8.8	6.8	11.0	8.3

Table 9.9: Table comparing the amount, composition and Alkali Index of the ash collected from the various runs of the fluidised-bed. Details of the contents of the initial fuel are also given; the initial ash content of the pellets is 34.27 %.

ULTIMATE ANALYSIS	COMPOSITION OF ASH FROM RUN (%)						INITIAL FUEL
	A	D	E	F	G	H	
C	18.46	24.08	14.76	13.40	15.75	-	41.56
H	0.34	0.25	0.22	0.22	0.21	-	3.19
N	0.34	0.35	0.25	0.21	0.29	-	1.76
S	1.60	1.49	1.57	1.51	1.90	-	2.09
Cl (mg/kg)	754	731	636	463	217	406	0.27 %
Remaining Combustibles	15.31	14.12	11.82	10.20	11.98	15.31	-

Table 9.10: Ultimate analysis of six ash samples; the remaining combustible material is also shown.

9.4 IMPACTS OF PELLET BINDERS ON COMBUSTION

Combustion tests were also undertaken in the fluidised-bed to investigate the impacts of the binders on the combustion behaviour of the pellets and the properties and composition of the flyash formed. This was especially important for the pellets containing the NaOH binder, as sodium is one of the alkali metals that contribute to slagging and fouling, by reducing the ash melting point. As the amounts required to improve pellet quality were small (considered in Chapter 7), however, they may not impact combustion significantly. Experiments were performed to compare the impacts of using no binder, to using 1 wt% of starch or caustic soda in the SMC-coal tailing pellets; each test was repeated. The combustion conditions were the same as those used for Case 1 above. The collection and analysis of the data from these experiments was the same as for manipulating the combustion variables, described in Section 9.2.3.

9.5 RESULTS AND ANALYSIS OF PELLET BINDERS

Where no binder was added to the air-dried SMC-coal tailing mixture – the control case – the operating conditions resulted in high temperatures towards the bottom of the reactor (870 °C) and high combustion efficiencies (95 %), with low NOx concentrations (23 ppm), as detailed above. The results for this case and those with the inclusion of the two binders in the air-dried pellets are compared in Table 9.11.

PARAMETER		BINDER		
		No Binder	Caustic Soda	Starch
Pellet Feedrate (kg/hr)		3.52	3.52	3.52
Primary Air (kg/m^{2}hr)		415	415	415
Secondary Air (kg/m^{2}hr)		165	165	165
Depth of Sand Bed (m)		0.22	0.22	0.22
Average Gas Concentration	CO_2 (%)	14.55	17.25	14.19
	O_2 (%)	3.95	1.40	2.21
	CO (%)	0.77	2.19	1.82
	NOx (ppm)	23.21	11.81	11.74
Combustion Efficiency, η_{CE} (%)		95.02	88.73	88.64
Average Temperature (°C)	Bed	869	844	844
	Above Bed	868	831	837
	Freeboard	505	383	461
Temperature Increase (°C/min)	Bed	2.64	2.07	2.60
	Above Bed	2.89	3.28	3.04
	Freeboard	1.92	1.53	1.71

Table 9.11: Combustion conditions and results from the tests assessing the effects of the two binders, compared to pellet combustion without a binder (control case).

9.5.1 Gas Concentrations, Combustion Efficiency and Temperatures

As can be seen, the use of the caustic soda and starch binders did alter the gas concentrations, where there were some discernible differences between these and the control. The O_2, CO_2 and CO concentrations for the starch case were most comparable to the control, while the results for the NaOH were less similar. In both instances, there was less O_2 present, resulting in increased levels of CO_2 and CO. As η_{CE} is based on these gas concentrations, as expressed in Eq. 8.1, there were also changes in these values. The increased amounts of CO for both cases resulted in markedly lower efficiencies (88.7 % compared to 95.0 % for the control). This may be due to an alteration in particle structure within the pellets due to the presence of the binders, or alternatively there is the possibility of additional gas-phase, chemical reactions between the binders and the air, preventing oxidation, resulting in higher CO and lower O_2 concentrations, reducing the overall η_{CE}. This is also the likely cause for the lower temperatures in the bed.

There were few impacts on the temperatures and the rates of temperature increase (Table 9.11). As with the tests where no binder was used, the maximum temperatures and the fastest rates of temperature increase were seen in and just above the bed (T2, y=0.20 m and T4, y=0.42 m respectively), where combustion was primarily taking place. The bed (T2), however, was slightly cooler for both binder cases, although the values were still within the standard deviation range (mean ± 1SD) of the control case. The rates of temperature increase were slightly slower within the bed (T2), but elevated above the bed (T4). The top of the freeboard (T7, y=1.54 m) was cooler for both binder cases, and for NaOH in particular. The temperature rise was also slightly slower here, due to the reduction in η_{CE}.

9.5.2 Acid Gas Emissions

Acid gas concentrations (NOx, SOx and HCl) produced during these tests were monitored, as above. Although there were differences between the control and the binder cases (Tables 9.11 and 9.12), the results for all species were low and thus there would appear to be little impact on the abundance of acid gas emissions. NOx concentrations varied between 7 and 48 ppm (10.9-74.6 mg/m^3) for all tests, where the average results for the binder cases were comparable but slightly lower. These concentrations were minimal – 10-20 ppm (15.5-31.0 mg/m^3), as predicted by previous literature and considered above. The comparison of such emissions to WID is reported subsequently.

AVERAGE SPECIES CONCENTRATION (ppm)	BINDER		
	No Binder	Caustic Soda	Starch
Chloride	5.33	1.11	2.02
Nitrite	0.30	<0.25	-
Nitrate	3.78	3.70	6.50
Sulphate	12.03	9.23	1.98

Table 9.12: Concentrations for acid gas species collected; comparison between the binders used.

The sulphur content of the initial fuel pellets was around 2.09 % (11,702 mg/kg). The amount of sulphates present in the flue gas by comparison were very low, particularly so when there were additions

of starch. This indicates that the SOx concentration was also likely to be minimal. As seen from Table 9.13, the sulphur was concentrated in the ash, as with the previous combustion tests, particularly so when the binders were included in the fuel. The Cl concentration in the initial fuel was 0.27 %. The chlorides present in the flue gas were low, specifically for the two binder cases, where Cl was concentrated in the ash, more so when the caustic soda binder was used.

9.5.3 Flyash Analysis: Properties and Composition

Flyash samples were collected from the cyclone after each test and a number of analytical techniques were employed to determine the elemental composition, the Alkali Index, the unburned carbon content and ash fusion temperatures. As above, a large proportion of the ash in the initial fuel remained as fine particulate ash, shown in Table 9.13. Of this, the unburned carbon content (remaining combustibles) was around 12 %, which was experimentally determined for each flyash sample. The results for previous tests were quite high and fairly constant for each case, resulting from inefficiencies primarily due to combustor limitations, as the primary air may have removed small particles, whether they were combusted or not. This was why the unburned carbon content was similar for each case, as the same air flowrates were utilised. The η_{CE} for the tests where binders were included were significantly lower than when no binder was used, as the binders made the pellets stronger and more durable, thus less dust formed during feeding. As the amount of unburned carbon in the ash samples from these tests was lower, it may suggest that the overall combustion efficiency was greater than calculated from these values alone.

COMPONENT (mg/kg)	BINDER			INITIAL FUEL
	No Binder	Caustic Soda	Starch	
Flyash as % of Ash in Pellets	79.0	83.3	75.5	-
Alkali Index (kg-alkali/GJ)	0.233	0.293	0.247	-
Unburned Carbon (%)	13.6	12.2	11.7	-
Al	44500	37250	46000	2500
Ca	67750	93000	92000	29680
Cl	560	1050	640	2700
Fe	38250	29500	33000	5604
K	20250	21500	27000	8364
Mg	8275	8250	9900	3485
Na	3775	14400	4100	1123
P	5650	6250	6800	3121
S	15225	25150	27000	11702
Si	3150	10150	7400	1487

Table 9.13: Table comparing the amount, composition and Alkali Index of the ash collected from the various cases compared to the composition of the initial fuel pellets.

The elemental composition of the flyash samples are shown in Table 9.13. This looked specifically for metal contaminants and those found in the largest amounts were aluminium, calcium, iron and potassium, although other elements, such as sulphur were also found to be concentrated here, when compared to the initial fuel; this was also found for the tests where no binder was included. A range of trace elements were also present, although as these amounts were small, they are not shown in the above table. The ash samples from the cases where the binders were included were very similar in terms of composition to the

control case. The sodium concentration for the caustic soda case, however, was greatly elevated compared to the control. The concentrations of Na and K form the elemental analysis were used to compute the Alkali Index. As shown in Table 9.13, the AI was found to be between 0.17 kg-alkali/GJ and 0.34 kg-alkali/GJ for the case where no binder was used; this indicates that fouling is probable, but not certain, as contemplated above. Comparable results were seen for the starch case. Due to the inclusion of the sodium for the caustic soda case, however, the AI of the ash from this test was much greater, as most of this alkali metal was collected in the flyash. Despite this, the value was still within in the limits noted above and did not cross the threshold of 0.34 kg-alkali/GJ into certain fouling. These results suggest that the Na and K concentrations from the fuel pellets alone are sufficient enough to result in the probable slagging and fouling in the system, caused by oxides of these metals. The values obtained for these fuels, even with additions of sodium from the caustic soda binder, were equivalent to fuels that are currently used, for example RDF, which has a AI value of 0.25 kg-alkali/GJ (Jenkins, *et al.*, 1998). A range of other biomass fuels have considerably greater AI values, such as switchgrass (0.65 kg-alkali/GJ), almond hulls (1.75 kg-alkali/GJ), rice straw (1.65 kg-alkali/GJ) and wheat straw (1.1 kg-alkali/GJ), as reported by Jenkins, *et al.* (1998). The AI computed assumed that all K and Na present in the ash was in oxide form.

The amounts of Si, Al and Fe were also ascertained from the elemental analysis (Table 9.13). As described above, high proportions of these metals in their oxide form can lead to slagging within the combustion system. As with the previous tests, the Al and Fe concentrations (29500-46000 mg/kg) were quite high, although Si was less abundant. There were however greater Si concentrations where a binder was included in the pellets, more so with caustic soda, further enhancing any issues with slagging and/or fouling brought about by the extra Na from this binder. P, S and Cl, which can also lead to the formation of detrimental compounds, were found to be concentrated in the ash for all tests. This, coupled with the AI results discussed above, show that slagging and fouling are likely to take place to some extent, simply due to the composition of the SMC and coal tailings, whether the caustic soda binder is included in the feed material or not.

The ash fusion temperatures for the samples, given in Table 9.14, can also give an indication of slagging and fouling. These showed that, as before, the inclusion of the caustic soda binder increased the likelihood of inducing these detrimental deposits to form in the combustor, by lowering the temperature at which the ash particles start to deform, melt and subsequently fuse together. Where starch or no binder was included, the temperatures for ash fusion were much greater. As can be seen, these two cases were similar and there was a greater difference between the hemispherical and fluid stages, unlike with the caustic soda case. The tolerances for these experimentally-determined temperatures can be quite high, up to 40 K within the laboratory and up to 80 K between laboratories, thus the differences between the cases may not be as significant as the results indicate. These values are however significantly higher than the bed temperatures outlined in Table 9.11, which would minimise fouling and agglomeration.

ASH FUSION TEMPERATURE (°C)	BINDER		
	No Binder	Caustic Soda	Starch
Initial Deformation	1160	-	1191
Hemispherical Stage	1246	1215	1244
Fluid Stage	1272	1226	1278

Table 9.14: Table showing the ash fusion temperatures of the flyash samples.

9.6 DISCUSSION

9.6.1 Air Ratio

Both manipulating the primary air flowrate and pellet feedrate, whilst other variables remained constant, altered the air ratio; values between 1.61 and 3.76 were investigated. There were significant and strong correlations between these variables, as expected (Figure 9.10). This had important ramifications on the nature of pellet combustion, and hence the alteration of the air ratio was found to be one of the most crucial factors influencing the exhaust gas composition and thus the combustion efficiency.

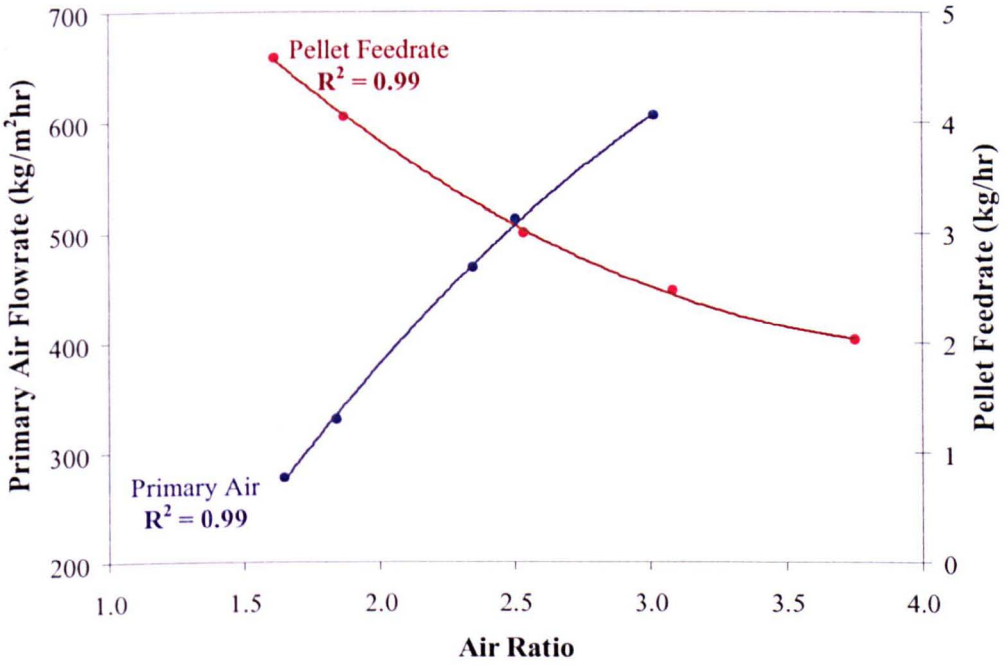


Figure 9.10: The relationship between the air ratio and the two dominating influences: the primary air flowrate and the pellet feedrate.

Figure 9.11 identifies the relatively strong relationship between the air ratio and the CO concentration; the greater the air ratio, the lower the CO concentration, due to the excess air allowing complete, rather than incomplete combustion. In addition to dramatically influencing the gas concentrations, the air ratio also had a clear relationship with the combustion efficiency, when the air ratio was altered both by manipulating the primary air flowrate and the pellet feedrate. These correlations indicated that the air ratio used in this combustor should be 2.5, so there is adequate excess air (150 %) to ensure that the efficiency is sufficient and the formation of detrimental emissions is minimised, whilst not allowing too much excess air into the system which could cool the reaction. Air ratios slightly lower than this resulted in dramatically lower combustion efficiencies, whereas air ratios slightly greater did not improve the

efficiency as significantly. It is unlikely that such conditions would be used on an industrial scale. As shown from Figure 9.11, there was often variations in the results (shown by the 95 % Confidence Limits) when the reactor was run under the same conditions. This was primarily due to the heterogeneity of the fuel and the variations in the air flowrates, as considered further below.

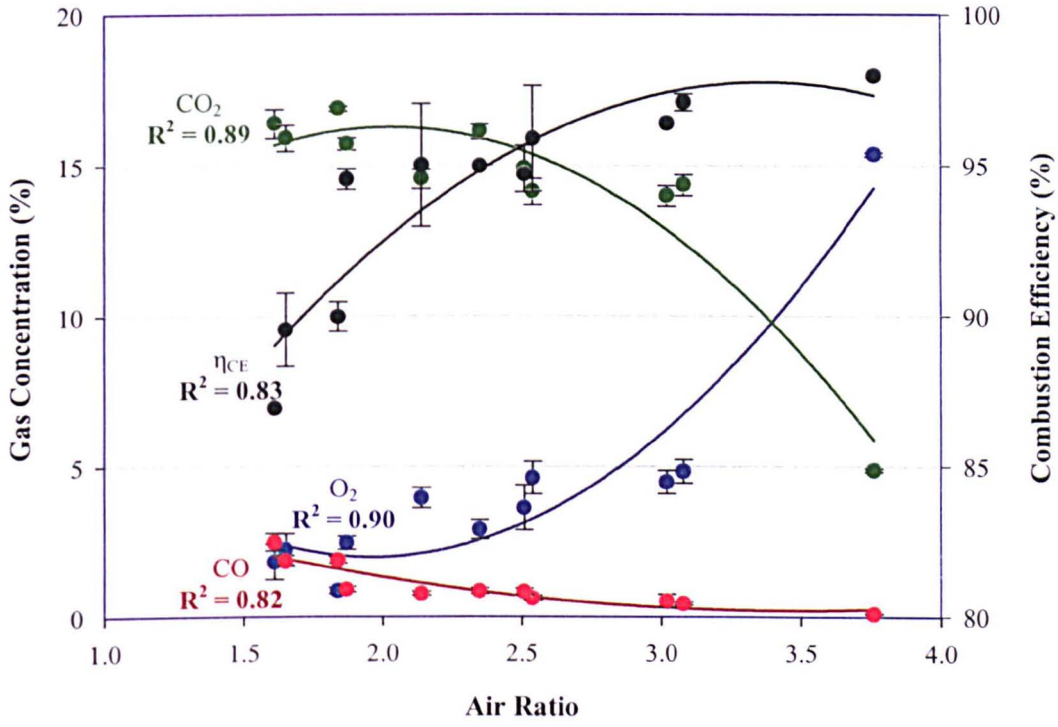


Figure 9.11: Correlations between the air ratio and (i) the exhaust gas concentrations and (ii) the combustion efficiency; this combines the results for both the variation of the pellet feedrate and the primary air flowrate.

9.6.2 Pellet Feedrate and Primary Air Flowrate

Data from when the pellet feedrate and primary air flowrate were manipulated produced very significant correlations with the parameters monitored. The results from both datasets, which indicate high η_{CE}, high temperatures and low pollutant concentrations were quite similar. Based on the pellet feedrate cases, these were achieved where the air ratio was 2.2-2.5 – a pellet feedrate of 3.0-3.5 kg/hr and a primary air flowrate of 460 kg/m^{2}hr. From the primary air cases, the best results were gained for a flowrate of 400-525 kg/m^{2}hr, with secondary air at 170 kg/m^{2}hr, where the pellet feedrate was 3.2 kg/hr.

9.6.3 Depth of the Sand Bed

As stated previously, it is difficult to form consequential relationships between the variables for the tests concerning the sand bed depth; there were, however, distinct differences between Cases 1 and 12. The η_{CE} was reduced by the deeper bed, as there was a vast increase in CO. Although the bed temperatures were similar, there was a marked reduction in freeboard temperatures, which would inhibit energy recovery. Furthermore, the reactor took longer to heat up as there was more bed material to heat. The bed depth-to-diameter ratio can indicate the likelihood of slugging in the bed, where high ratios suggest this phenomenon is likely. Here, the combustion chamber was small and the bed diameter was 0.15 m.

Bed depths of 0.30 m for the preliminary investigation (depth-to-diameter ratio of 2.0), 0.22 m for Case 1 (ratio of 1.47) and 0.27 m for Case 12 (ratio of 1.8) were used.

9.6.4 Impacts of the Binders

Pellet combustion was affected by the presence of starch and caustic soda. Whilst starch significantly improved pellet quality, it impacted the gas concentrations in such a way that η_{CE} was reduced by 6 %; NaOH had a similar influence, although there were slightly lower amounts of combustible material in the ash for both cases. The temperatures and ash composition of the control, where no binder was used, were comparable to the inclusion of 1 wt% starch. This is therefore a suitable additive for these fuels. Caustic soda on the other hand did impact the ash composition and increased the likelihood of slagging/fouling. Furthermore, the improvements in pellet quality with the additions of NaOH were not as apparent, and given that this also detrimentally impacted combustion, it is not appropriate for this application.

9.6.5 Temperatures and Rate of Temperature Increase

The maximum temperatures achieved in all cases were in and just above the sand bed (T2, y=0.20 m and T4, y=0.42 m respectively), both above 850 °C (averages of 834-887 °C for T2 and 825-892 °C for T4). The high volatile contents of the SMC, as noted in the literature review and as experimentally-determined here, resulted in its rapid combustion, primarily in the bed, heating this section. The freeboard (T7, y=1.54 m) was considerably cooler for all cases and also varied much more, 423-577 °C depending on the conditions. For the cases where the pellet feedrate increased, the temperatures throughout the reactor also increased in a fairly linear manner (Figure 9.5); the primary air cases also showed a significant trend, where the temperatures increased with air flowrates until a critical value was achieved (450-500 kg/m^{2}hr), whereupon the temperatures decreased, cooled by the excess air (Figure 9.8). There appeared to be little correlation between the temperatures and air ratio. As commercial-scale combustion is used for energy recovery, the temperatures need to be sufficiently high to be able to create steam to drive a turbine. The temperatures here were adequate for energy recovery and suitably high to generate the heat and/or power required, providing appropriate conditions were employed. They were comparable, towards the high end of the range, to the fluidised-bed combustion of other fuels (discussed below). Furthermore, the reactions were self-sustaining, not necessitating the use of secondary or supplementary fuels. Even though the excess air provided to achieve optimum fuel burn out was high, this did not appear to cool the reactions until high air flowrates were achieved, however, lowering the air ratio would increase the temperature.

The initial rate of temperature increase was also noted for each case and was more rapid in and just above the bed (T2 and T4). The rate of increase was significantly slower for the freeboard for all cases. There are two primary reasons for the temperature increases being more rapid in the bed and the bed being warmer than the freeboard. The first is due to the fact that the fuel was pelletised, and thus dense, so it could burn in the bed, rather than in the freeboard. Secondly, the high volatiles content of the SMC, as noted above, resulted in rapid combustion in the bed leading to a faster heating rate here.

9.6.6 Gas Concentrations and Combustion Efficiency

There were significant correlations between the O_2, CO_2 and CO concentrations and the variables manipulated and thus also with the air ratio. These followed distinct trends when plotted against the increasing pellet feedrate. The correlation for CO and the air flowrate was also significant, although the plots for CO_2 and O_2 were not. Despite this, a good relationship was still found between the air flowrate and combustion efficiency. The variation in O_2 was quite dramatic, and was closely matched with the air ratio; for extremely air-rich environments, the O_2 concentration peaked at over 15 %, whereas for less air-rich environments, the concentration was 0.86 %. CO_2 also varied radically with air ratio (4.87-16.89 %); O_2 and CO_2 closely mirrored each other. CO concentrations were low, 0.10-2.47 %, indicating that some incomplete combustion took place where less excess air was present. The η_{CE} ranged from 86.93 % to 97.98 %; high efficiencies could be achieved using optimal conditions within the reactor. It has also been shown that if the conditions were not appropriate, for example low air ratios, then η_{CE} was considerably reduced, leading to the formation of unwanted pollutants. Although the results indicate that η_{CE} can be quite high, ways in which it can be further improved are considered below.

9.6.7 Acid Gas Emissions: NOx, SOx and HCl

NOx emissions did not follow a trend and appear to not have a relationship with any of the variables tested or the other data collected. These emissions however were quite minimal from the oxidation of fuel nitrogen, due to the inorganic origin (nitrates) of the majority of N. The NOx species formed are likely to be from a thermal source, as air was used instead of O_2, although some may be from a prompt source, if hydrocarbon fragments reacted with nitrogen in fuel-rich areas, due to insufficient mixing; these mechanisms were described in Section 3.4.1. These data corroborate the results from both the initial investigation into pellet combustion and previous literary sources (Williams, 2001; Williams, *et al.*, 2001a; Chugh and Patwardhan, 2004). As the N here was not found to be concentrated in the ash, it is likely that N_2O formed instead. SOx and HCl emissions were also found to be low, in accordance with the previous literature and the initial investigation. The large quantities of S and Cl in the ash explain the low SOx and HCl exhaust gases concentrations. NOx, SOx and HCl emissions from these tests are compared to WID in the subsequent chapter, to ensure legislation is met.

9.6.8 Flyash Properties and Composition

The majority of the ash was found in the exhaust gases and collected in the cyclone, thus it is clear that particulate removal will be required. From computing the AI, it was found that the concentrations of Na and K were sufficient enough to result in the probable slagging and fouling of the system, caused by oxides of these metals, whether or not additional Na was included in the binder. This assumed that all the K and Na present were in oxide form. Many elements were found in considerable concentrations in these ash samples, namely Al, Ca, Fe, K, Mg, Na, P and S, although a range of trace elements were also identified. Whilst a number of these cause slagging, fouling and ash agglomeration, which were found to be the most common elements, the fusion temperatures were lower than those generated in the reactor.

9.6.9 Determining the Optimum Operating Conditions

Based on the results of SMC-coal tailing pellet combustion, optimum values for the main variables (the operating conditions) were determined for this rig, shown in Table 9.15, based on the optimum air ratio. As an optimum air ratio was required to ensure combustion was efficient in this combustor, the pellet feedrate and primary air flowrate were therefore manipulated to achieve this. The above discussion in Section 9.6.2 suggests a minimum air ratio of 2.5 should be used; hence at least 150 % excess air. Based on this, a pellet feedrate of 185 kg/m^{2}hr (equal to 3.25 kg/hr) and a total air flowrate of 650 kg/m^{2}hr (primary air at 480 kg/m^{2}hr with 170 kg/m^{2}hr of secondary air) could be used to achieve an air ratio of 2.6 (160 % excess air). The values of the pellet feedrate and primary air flowrate both fit within the ideal limits discussed above in Section 9.6.2. Table 9.15 also shows predictions for the temperatures and gas concentrations, based on an extrapolation of the experimental results obtained from cases where the bed depth was 0.22 m, the most favourable value for this parameter.

PARAMETER		OPTIMUM
Pellet Feedrate (kg/hr)		3.25
Primary Air (kg/m^{2}hr)		480
Secondary Air (kg/m^{2}hr)		170
Depth of Sand Bed (m)		0.22
Air Ratio		2.6
Gas Concentration	**CO_2 (%)**	14.98
	O_2 (%)	3.57
	CO (%)	0.60
Combustion Efficiency, η_{CE} (%)		96.12
Temperature (°C)	**Bed**	865
	Above Bed	870
	Freeboard	519

Table 9.15: Predictions for the gas concentrations, combustion efficiency and temperatures for the optimum pellet feedrate and primary air flowrate, based on an ideal air ratio of 2.6.

Although such operating conditions only apply to the specific combustor used, there are implications for the industrial, larger-scale combustion of this fuel; these would mean optimising the burner further to improve the results, namely the combustion efficiency and thus the energy recovered. The first one is the scaling-up of the reactor and the second is the introduction of secondary air jets. The negative impacts from the additions of the binders may not be as apparent using these improvements. Firstly, although the results indicate that η_{CE} can be quite high, due to the small-scale nature of the reactor, this could be significantly increased by scaling-up the combustor to a practical scale plant. This would mean a deeper bed could be utilised, whilst maintaining a depth-to-diameter ratio near to 1, to ensure proper fluidisation is achieved. Furthermore, when the scaling-up of laboratory-scale results is employed to predict the behaviour of industrial-scale combustion plants, it is usually found that combustor performance is enhanced and the use of a deeper bed will further improve the efficiency. These results indicate that η_{CE} for these pellets is already quite high, thus optimising the operating conditions of an industrial reactor could ensure the efficiency achieved is increased further, by limiting CO in the reactor.

Secondly, the addition of high-speed, turbulent secondary air jets in appropriate locations, which would undoubtedly be included in an industrial reactor, could be beneficial in improving combustion in many ways (Granada, *et al.*, 2006). Circulation would be enhanced to optimise fuel-oxidiser mixing within the system, to redistribute any excess oxygen and facilitate the burnout of fuel and residual gases. η_{CE} would thus be increased, achieved by reducing the CO concentrations (by completing oxidation) and limiting the combustible material in the ash. Turbulence within the reactor will also help to avoid cold and/or hot spots or fuel-rich zones, which could further impede prompt NOx formation. Moreover, this secondary air would mean a lower air ratio could be used, to improve temperature profiles and maintain those necessary for energy recovery throughout the reactor. As described above, large air ratios were required for this reactor to ensure high η_{CE}, as there were no secondary air jets. For an industrial combustor, an air ratio of 2.6 would significantly reduce gas temperatures and thus encumber energy recovery. It is essential to maintain high temperatures to generate energy, hence it is vital to take this into consideration when determining the optimum conditions. However, these conditions would be unsuitable for a large EfW facility, even though they were appropriate for the laboratory-scale combustion of such wastes.

9.6.10 Comparison to the Fluidised-Bed Combustion of Other Fuels

These results have been compared to those of other fuels in similar combustors, as fluidised-beds are used to combust a variety of fuels, ranging from fossil fuels, such as various ranks of coal, to industrial and biomass wastes, for example meat and bone meal and olive oil industry residue, as well as energy crops like sorghum and poplar. Table 9.16 compares the operating conditions, emissions, efficiency and temperatures for several studies; many of these were considered in great detail in Section 4.5.

Excess air (fuel-lean conditions) was used in all cases for SMC-coal tailing pellet combustion, to ensure high carbon burn-out and good efficiencies were achieved. It was suggested that approximately 160 % excess air (air ratio of 2.6) should be utilised, which is significantly higher than those reported for other fuels in the literature. This may be due to the nature of the pellets, but is more likely to be due to the small-scale nature and design of the experimental combustor. When these pellets are combusted on a commercial scale, however, secondary air jets may enhance combustion; therefore the amount of excess air could be decreased. Even though so much excess air was required to achieve good levels of efficiency, the temperatures of the reactions still remained high. Some of the experiments described used 6 % excess oxygen in the system; for the cases herein, the excess oxygen present was generally 1-5.5 %, although for extremely high air-to-fuel ratio cases (3.76) where the pellet feedrate was low, around 15 % oxygen was present. This did result in a very high value for η_{CE}. This was also calculated for many of these investigations; not all however were the carbon combustion efficiency (η_{CE}). The overall net efficiency for the entire system based on either the LHV or the HHV was computed in some cases, which is why these values are particularly low. Efficiency for SMC-coal tailing pellet combustion ranged from 86.93 % to 97.98 % and corresponds well to those achieved from the variety of other fuels available for this purpose, as values reported in the literature had a wider range (85.8-99.8 %).

REFERENCE	TYPE	FUEL(S)	AIR RATIO/ EXCESS AIR	FLUIDISING AIR	EMISSIONS	COMBUSTION EFFICIENCY	TEMPERATURE
Desroches-Ducarne, *et al.* (1998)	CFB	coal and MSW	70 % excess air	-	CO: ~ 0.87 % NO: 80 – 160 ppmv SO_2: 20 – 440 ppmv HCl: 40 – 420 ppmv	-	800 °C
Armesto, *et al.* (2002)	BFB	rice husks	6 % excess O_2	1 – 1.2 m/s	CO: 1194 – 1808 mg/Nm^3 NOx: 100 – 430 mg/Nm^3	> 97 %	840 – 880 °C
Armesto, *et al.* (2003)	BFB	olive oil industry residue and coal	6 % excess O_2	0.7 – 1 m/s	N_2O: 100 – 180 mg/Nm^3 SO_2: 400 – 1000 mg/Nm^3	88 – 99 %	830 – 870 °C
Henihan, *et al.* (2003)	-	poultry litter and peat	5 – 12 % (bed)	-	CO: 50 – 400 ppm NO: < 120 ppm N_2O: < 25 ppm	-	750 - 850 °C (bed)
Çubuk and Heperkan (2004)	-	sweet sorghum and lignite	-	12 m^3/hr	CO: 2730 – 3400 ppm NOx: 201 – 222 ppm SO_2: 625 – 730 ppm	95.2 – 95.7 %	~ 850 °C
Gayan, *et al.* (2004)	CFB	coal and pine bark	18 – 25 %	4 – 6 m/s	CO: 100 - 400 ppm	96 – 99.8 %	800 - 900 °C
Cummins, *et al.* (2006)	BFB	peat with meat and bone meal	~ 6 % O_2	96 Nl/min	CO: 24 mg/Nm^3 NOx: 110 mg/Nm^3 SO_2: 146 mg/Nm^3	-	882 °C (bed)
Fryda, *et al.* (2006)	BFB	meat and bone meal, coal and olive bagasse	1.2 – 1.6	0.55 – 1.52 m/s	CO: 100 – 1150 ppm NOx: 250 – 650 ppm SO_2: 250 – 315 ppm	85.8 – 99.2 %	~ 875 °C (bed)
Huang, *et al.* (2006)	PFB	coal, biomass and biomass wastes	-	-	NOx: 122 - 184 mg/Nm^3 SOx: 125 – 191 mg/Nm^3 HCl: 85 – 275 mg/Nm^3	net: 41 – 43.5 % (based on HHV)	~ 855 °C (bed)
Llorente, *et al.* (2006)	BFB	Brassica, thistle and almond shells	~ 60%	1.2 m/s	-	> 98 %	775 °C (bed)
McIlveen-Wright, *et al.* (2006)	CFB	coal, biomass and plastic waste	20 %	-	CO: 60.9 – 62.3 mg/Nm^3 NOx: 345 – 352 mg/Nm^3 SO_2: 246 - 257 mg/Nm^3	net: ~ 38% (based on HHV)	-
Llorente and Cuadrado (2007)	BFB	poplar	60 – 70 %	1.1 – 1.3 m/s	-	96.3 – 96.7 %	775 – 850 °C (bed)
McIlveen-Wright, *et al.* (2007)	CFB	coal, biomass and biomass waste	-	-	NOx: 145 - 280 mg/Nm^3 SOx: 60 - 450 mg/Nm^3 HCl: 60 - 110 mg/Nm^3	net: 28.2 – 44 % (based on LHV)	480 – 538 °C

Table 9.16: Table comparing data concerning the operating conditions and key results (emissions, efficiency and temperatures) from various studies of biomass combustion in different types of fluidised-bed rectors. Key: CFB = circulating fluidised-bed; BFB = bubbling fluidised-bed; PFB = pressurised fluidised-bed.

Results for emissions, such as CO, HCl, NOx and SOx, or specific species for the last two, were reported for the tests outlined in Table 9.16. Desroches-Ducarne, *et al.* (1998) found that CO accounted for around 0.87 % of flue gas emissions for the combustion of coal and MSW, which is within the range of 0.1-2.5 % for SMC-coal tailing pellets. Other research also details CO emissions, which range widely for different fuels; coal co-fired with pine bark and peat co-fired with meat and bone meal both produced minimal CO, whereas rice husks produced more significant concentrations in a bubbling fluidised-bed (Armesto, *et al.*, 2002; Gayan, *et al.*, 2004; Cummins, *et al.*, 2006).

Chloride species produced from SMC-coal tailing pellets were low. Desroches-Ducarne, *et al.* (1998), Huang, *et al.* (2006) and McIlveen-Wright, *et al.* (2007) also monitored HCl for the combustion of their fuels; the concentrations in the exhaust gases were low, although Desroches-Ducarne, *et al.* (1998) suggested that the presence of HCl, even in concentrations as low as 220 ppm can inhibit CO oxidation. Huang, *et al.* (2006) found that as Cl in the fuel feed increases, HCl emissions also increase; willow chips, switchgrass and olive pits, which contained no Cl produced less than 100 mg/Nm^3 when co-fired with coal (0.14 % Cl) in 6 % excess oxygen, whereas the miscanthus and straw, containing 0.25 % and 0.28 % respectively produced 275.8 and 285.5 mg/Nm^3 when co-fried in the same ratio. NOx emissions from SMC-coal tailing pellet combustion were in the region of 2-58 ppm, which, as suggested from previous literature, was minimal. The NOx concentrations for the combustion tests herein correspond well with, and in most cases were lower than, the results of Desroches-Ducarne, *et al.* (1998), Henihan, *et al.* (2003), Çubuk and Heperkan (2004) and Fryda, *et al.* (2006); the highest value for NOx species was 650 ppm, from the combustion of lignite, meat and bone meal in a bubbling fluidised-bed with an air ratio of 1.52, as investigated by Fryda, *et al.* (2006). SO_2 emissions were observed for the combustion of various fuels. These all report fairly low values, up to 730 ppm for sweet sorghum-lignite blends (Çubuk and Heperkan, 2004). Total SOx were also monitored in some cases and note low concentrations, as for the combustion of SMC-coal tailing pellets (Huang, *et al.*, 2006; McIlveen-Wright, *et al.*, 2007).

Lastly, the temperatures achieved, particularly those in the bed were comparable to those discussed in the literature. The bed temperatures here were generally above 850 °C, which is consistent with the range of 775-900 °C for the studies considered. Many of these papers, including Armesto, *et al.* (2002) and Fryda, *et al.* (2006), report that the temperatures achieved in the freeboard of bubbling fluidised-beds are considerably lower than those of the bed (475-600 °C), which is again similar to the findings here, where freeboard temperatures were generally below 500 °C. Henihan, *et al.* (2003), however noted that the freeboard temperatures were greater than those in the bed: 930-950 °C, as opposed to 750-850 °C in the bed. Llorente and Cuadrado (2007) also reported similar results for a bubbling fluidised-bed.

9.6.11 Discussion of Experimental Measurement Accuracy and Errors

The accuracy of the experimental readings was likely to be one of the main sources of error in the data obtained from these tests. As a range of equipment was required to control the variables and record data

concerning temperatures and gas concentrations, there were several sources of error which may impact on the results. Furthermore, the ash analysis had its associated errors. These will be assessed in turn. A number of rotameters were used to monitor the propane and primary and secondary air flows, where different sizes were employed depending on the magnitude of the flowrate, to minimise errors. For low flowrates, such as for the propane, a small rotameter was used, whereas large and medium rotameters were used for the primary and secondary air respectively, as considered in Section 8.5.2.3. Despite these measures, the air flowrates were not constant and unfortunately could not be controlled further. The disparity in these readings was likely to affect the air ratios calculated and thus produced discrepancies in the results. There were variations in data, particularly for the gas concentrations, when the reactor was run under the same conditions, as seen from the 95 % confidence limits in the graphs throughout this chapter. Additionally, the variation of the pneumatic feeder would lead to further inaccuracies in the calculation of the air ratio. This also assumes that the pellet composition is uniform, whereas in practice, the mixing of the two different fuels within the pellets will lead to the uneven distribution of each within the pellets, resulting in variations in CV and air ratios computed. This may also be due in part to the heterogeneity of the SMC.

The temperatures monitored did not exceed the range of the thermocouples and the errors associated with this degree of accuracy (± 0.75 °C) were not problematic for the purpose intended here, although these were not corrected for radiation. The gases emitted from the exhaust passed through a glass wool filter before going to the ADC MGA300 or Signal Series 4000 NOx analysers; as there was often a substantial amount of tubing required to connect the reactor to the analyser, there may have been considerable time lags and potential leaks, which means that gas readings may not have been entirely precise. The accuracy of the final readings also depended on the calibration gases used. Any inaccuracies here will have impacted the combustion efficiencies calculated, as this depended on these gases concentrations. The capture and chromatographic analysis of SO_4^{2-} and Cl^- species also had its associated errors, therefore the values may not be entirely representative. The low values obtained herein, however, for NOx, SOx and HCl were corroborated by both the high concentration of the species in the ash that would cause these acid gases (S and Cl) and also by the previous investigations. Whilst the absolute values recorded and reported here may not be entirely accurate, the magnitude of these values is thought to be precise and thus representative of those which could be expected from the industrial-scale combustion of these wastes.

The analysis of the ash also has errors; the balance used to weigh the ash had a high accuracy of ± 0.05 g, although the accuracy of the titrations using nitric and hydrochloric acids may be more questionable. The precision of this method was good, however, as there was little variation between the composition of the ash samples. Other tests concerning the ash however are known to be inaccurate; namely the ash fusion tests, as considered previously. The results often have a high percentage error, which makes the reliability of the results somewhat controversial, especially since the differences in the results were only just above the tolerances reported. The tests were repeated for each case to minimise these discrepancies.

Another reason why these tests could be unreliable is that the behaviour of the ash may be different in the laboratory, compared to in an industrial appliance and therefore such tests would need to be repeated when larger-scale experiments are carried out.

9.7 CONCLUSIONS

From the initial investigation into the possibility of thermal treatments for SMC and coal tailings, it was found that combustion in their pelleted form produced the best results in terms of combustion efficiency; furthermore, combustion in a fluidised-bed was significantly better than a packed-bed. Hence, SMC-coal tailing pellet combustion in a laboratory-scale fluidised-bed was the primary focus of the further experiments. From the results of such investigations, the following conclusions can be drawn. The SMC-coal tailing pellet feedrate had a significant impact on the temperatures and gas concentrations, and also on the combustion efficiency; a range of values were examined (2.02-4.58 kg/hr) and based on these, the optimum pellet feedrate should be 3.25 kg/hr. The primary air also had a significant impact on the temperatures within the reactor, both in the bed and freeboard; the effect on the gas concentrations was less apparent, although was still clear for the combustion efficiency. Through investigating a range of primary air flowrates (277-606 kg/m^2hr), the most appropriate value was 480 kg/m^2hr. The air ratio within the fluidised-bed needed to be at least 2.5 (i.e. 150 % excess air) to ensure the efficiency achieved during combustion was sufficient. It was also necessary to have adequate excess air to minimise harmful species in the exhaust, such as CO. The lower bed depth of 0.22 m produced better results than a bed of 0.27 m, in terms of gas concentrations, combustion efficiency and temperatures, although it is difficult to make assumptions and further generalisations based on only two conditions.

Acid gas emissions (NOx, SOx and HCl) were found only in limited concentrations since the majority of these species remained in the ash, as predicted from the work of others; nitrogen was not found in such significant concentrations in the ash, thus N_2O is likely to have formed, a common drawback of fluidised-bed combustion. Whilst the combustion efficiencies from the gas concentrations were high, the ash analyses suggested considerable combustible material remained. The high fusion temperatures of the ash produced from the combustion of these fuel pellets is unlikely to cause fouling and/or slagging in the system, despite the presence of alkali metal oxides and other species that may cause such issues, as the combustion temperatures were much lower than the ash fusion temperatures. The majority of flyash was found as small particulates, thus some form of particulate collection will be required before the exhaust can be emitted to the atmosphere. Ways in which combustor performance could be enhanced were also considered, such as scaling-up the reactor. The inclusion of secondary air to aid mixing in the combustor would also be beneficial in improving the η_{CE}, increasing temperatures and minimising CO, whilst limiting the need for large amounts of excess air, which can cool reactions.

10

INDUSTRIAL IMPLICATIONS

10.1 INTRODUCTION

Numerous pellet combustion tests were completed in a laboratory-scale atmospheric, bubbling fluidised-bed under a range of conditions. A mathematical model, FLUENT was used to evaluate the suitability of replicating the experimental data and to investigate particle elutriation and entrainment. Additionally, heat and power generation from these wastes was also explored for a theoretical furnace, boiler, dryer and steam turbine configuration. Mass and energy balances were completed, based on various fuel feedrates to enable the calculation of steam properties and electrical outputs. Furthermore, the ability of this thermal treatment to comply with legislation is considered, where the emissions produced were compared to WID. Lastly, the economics involved with reusing these wastes are evaluated, relating to sourcing and processing the materials, pelletising the wastes into a usable fuel, and storing and using the pellets.

10.2 FLUENT MODELLING

10.2.1 FLUENT Modelling Code

FLUENT is a computational fluid dynamics (CFD) code used for mathematically modelling gas flows and gas-phase reactions and thus has a variety of applications. Initially, a broad introduction to modelling is given here, followed by a specific focus on FLUENT – both its purposes and features, which are then utilised to perform simulations regarding the experimental data gained from the previous chapters.

10.2.1.1 General Introduction to Modelling: Approaches and Techniques

Models, simplifications of reality, have been devised to aid our understanding of the complexity of actual situations, such as the combustion behaviour of fuels within a reactor. Whilst they are sometimes

criticised for oversimplifying matters and omitting essential features, this does not mean they are of no use, or do not provide any advancement of our comprehension of combustion systems.

As with models in all areas of science and engineering, they can be categorised according to their approaches and applications, although classification can be somewhat complicated by overlapping definitions of some types. Conceptual models, mental abstractions, rely on the method of analogy, whereas numerical or mathematical models, such as FLUENT, can be used to obtain formulaic relationships between certain aspects of the combustion system. Theoretical models use deductive reasoning, while empirical models utilise experimentation. A physical or hardware model involves the creation of a replica, usually to scale. These different model types can be used together, known as system-based, to link various models or systems. Each approach has its relative merits; the main problems are in the applicability of models and the relevancy of their results, which is common to all models. Even if accuracy and precision are sufficient, which is not necessarily the case, whether the results are useful is another matter. Even if they are, it is important to realise where they can be applied, essentially not extrapolating beyond the data on which the model is based – for example, applying to alternative fuels or reactors. Model testing can also be difficult, as data are usually required; thus, the model is only as good as the inputs supplied. Additionally, data constraints, where data are unavailable, mean models cannot be tested. In other cases, the model may be too advanced for the data available.

10.2.1.2 Overview of FLUENT and Its Applications

The FLUENT CFD code is concerned with gas flows and thus can mathematically model the gas phase during SMC-coal tailing pellet combustion within a fluidised-bed, by simulating reactions. GAMBIT, another software package, is used to produce a 'mesh' using the geometric information concerning the combustion chamber. FLUENT is able to model the fluid flow and the heat transfer for a particular geometry during combustion – in this case the laboratory-scale, fluidised-bed reactor – producing a numerical solution to these equations. The geometry can be specified using GAMBIT, the programme used herein, or a range of other computer-aided design packages, to create a 2D or 3D grid/mesh for CFD applications. GAMBIT enables a model of the reactor to be built and meshed. Specific types of boundaries, such as velocity inlets and pressure outlets, can be assigned to various parts of the geometry. Once the relevant mesh has been established, it can be exported and then read into the FLUENT programme, after which the solver formulation is selected and the basic equations are chosen. Subsequently, the boundary conditions and fluid properties are defined and the calculations can be executed to find the solution to the problem.

10.2.1.3 Using FLUENT: Software Features and Menus

FLUENT has a series of menus and a set of subsequent functions in each. Generally, there are five stages necessary to obtain results after the initial geometry has been created; these are considered in relation to the menus and main commands that were selected or altered from the default settings delineated.

STAGE 1. Once the mesh has been established, it can be read into FLUENT and set-up.

STAGE 2. The problem to be solved for the particular geometry is outlined, after which the solver formulation is selected and the basic equations are chosen.

STAGE 3. The boundary conditions and fluid properties are defined.

STAGE 4. A series of calculations (iterations) are executed by the model, until convergence is achieved to find the numerical result.

STAGE 5. The solution acquired from the iterations can then be used to obtain meaningful results concerning the problem specified.

Stage 1 requires the use of the 'FILE' and 'GRID' menus, whereby the geometry (saved in GAMBIT as a 'mesh' file) can be imported and then scaled to SI units and orientated the correct way. Also in the 'GRID' menu, the mesh can be smoothed and swapped ('SMOOTH/SWAP'), until no nodes move, smoothing is complete and no faces are swapped. Lastly in this menu, the mesh can be checked, to ensure that the domain extents and the volume and face area statistics are correct.

Stage 2 uses the 'DEFINE' menu to select the equations that require solving for the problem at hand. Within this menu, there are numerous sub-menus, and functions within these. The first of the four main sub-menus is 'MODELS', within which there is a list of 8 further commands, consisting of: 'SOLVER': where the space, time and velocity formulation can be assigned; 'MULTIPHASE': where multiphase flow equations are specified; 'ENERGY': where the energy equation can be included, as it is *not* by default; 'VISCOUS': where turbulence models can be included, as laminar flow is the default option, and near-wall functions are selected; 'RADIATION': where radiation energy transfer can be included; 'SPECIES': where molecule species transport and reaction equations can be selected, including the properties of the material mixture and the turbulence-chemistry interaction; 'DISCRETE PHASE': where the particle treatment and interaction can be included, concerning the physical model and particle tracking; and 'SOLIDIFICATION AND MELTING': which are not selected by default. The second sub-menu concerns 'MATERIALS'; the default is air, but the type and specific material can be selected from the large database. Various material properties can also be specified. Thirdly, the 'OPERATING CONDITIONS' are defined, where the pressure is outlined and gravity (if it is included) is set. The last of the primary menus used within the 'DEFINE' menu is 'BOUNDARY CONDITIONS', which can subsequently be identified, relating to the specific types of boundaries denoted in the GAMBIT model; momentum, material species and thermal properties can be assigned to each boundary.

Stages 3 and 4 make use of the functions provided in the 'SOLVE' menu, where the parameters are set for the problem and it can be initialised and iterations performed. There are several sub-menus and subsequent commands within this. The first is 'CONTROLS – SOLUTION', where equations are selected and choices regarding the under-relaxation factors and pressure-velocity coupling are made. Also within this menu, the discretization parameters are expressed, in terms of pressure, momentum, turbulent kinetic energy, turbulent dissipation rate, the material species selected and the energy. The second menu is 'INITIALIZE – INITIALIZE', where estimations are made for the variables selected,

namely pressure, velocity, energy and temperature. Where the problem is time-dependent, this stage allows the initial conditions to be identified. Within the 'MONITORS' menu, there are several functions that can be performed. The first of these is 'RESIDUALS' to print or plot the residuals concerning the velocity, energy or species with regard to the convergence criterion. The second is 'FORCE' to monitor those acting upon the wall in terms of lift, momentum or drag coefficients. 'SURFACE' and 'VOLUME' options allow similar functions to be monitored, with regard to the surface or domain volume integrals, either over time or for a certain number of iterations. Different surfaces or cell zones can be specified, for which the field variable can be pressure, density, velocity, temperature, radiation or turbulence, among others. 'EXECUTE COMMANDS' allows automatic plotting over time or iteration, providing a plot of contours, pathlines, vectors, and so on of pressure, density, velocity, temperature, etc., already expressed in the 'DISPLAY' menu. Lastly, the 'ITERATE' facility permits the number of iterations to be specified and begins these to solve the overall problem.

Stage 5 uses the 'SURFACE', 'DISPLAY', 'PLOT' and 'REPORT' menus to identify meaningful results. The first of these allows for the definition of points, lines and surfaces to be created/specified within the geometry, from which key results can be specified. The second, 'DISPLAY', is used for presenting the data graphically, for example, as a grid within the geometry, as contours or vectors on a specified surface or as pathlines/tracks of fluid or solid particles. From the 'PLOT' menu, 2-D charts can be created using data gained from the solved problem. Finally, within the 'REPORT' menu, fluxes (concerning mass, heat or radiation flowrates), forces and surface or volume integrals can be detailed, over time or iteration.

10.2.2 Mesh Geometry Formation Using GAMBIT

The mesh of the combustor geometry was created using GAMBIT. The reactor was modelled, where the gas flows would be, resulting in a geometry of the chamber from above the sand bed to the top of the combustor, including the exhaust duct – the connection with the cyclone. This occurred in three phases: (i) the geometry was created; (ii) the geometry was meshed; and (iii) the boundary types were specified. These stages are outlined below. Where a specific boundary type is not assigned to a part of the geometry, it is taken that the section is a 'wall', i.e. there is no flow. More specific details can be defined when the completed geometry is read into FLUENT.

In order to complete first phase, a 208 cm long cylinder, with a radius of 7.5 cm was created in the positive Y direction (Volume 1); these dimensions were later scaled when the meshed geometry was read into FLUENT. The exhaust pipe was modelled, where a 15 cm-long cylinder with a radius of 3.5 cm was created in the positive X direction and united with the first cylinder 5 cm from the top, forming the exhaust. A face was then added 17 cm from the top of the main cylinder, in the ZX direction and the entire geometry was then split into two separate volumes, using this boundary. The bottom section (Volume 1), where the majority of combustion reactions were taking place, would later be given a fine mesh, and the smaller, top section (Volume 2) would have a coarser mesh, as fewer reactions would be

occurring here (Figure 10.1). The geometry was split further by adding a face in the YZ direction, which was used to halve Volumes 1 and 2. The exhaust pipe was also split into a separate volume (Volume 3), and another face was added in the XY direction to halve the exhaust lengthways. Compared to the schematic of the laboratory-scale fluidised-bed in Figure 9.1, the modelled geometry was simplified, to avoid issues concerning the joints with the feeding tube, ignitor and the pipe to the viewing lens.

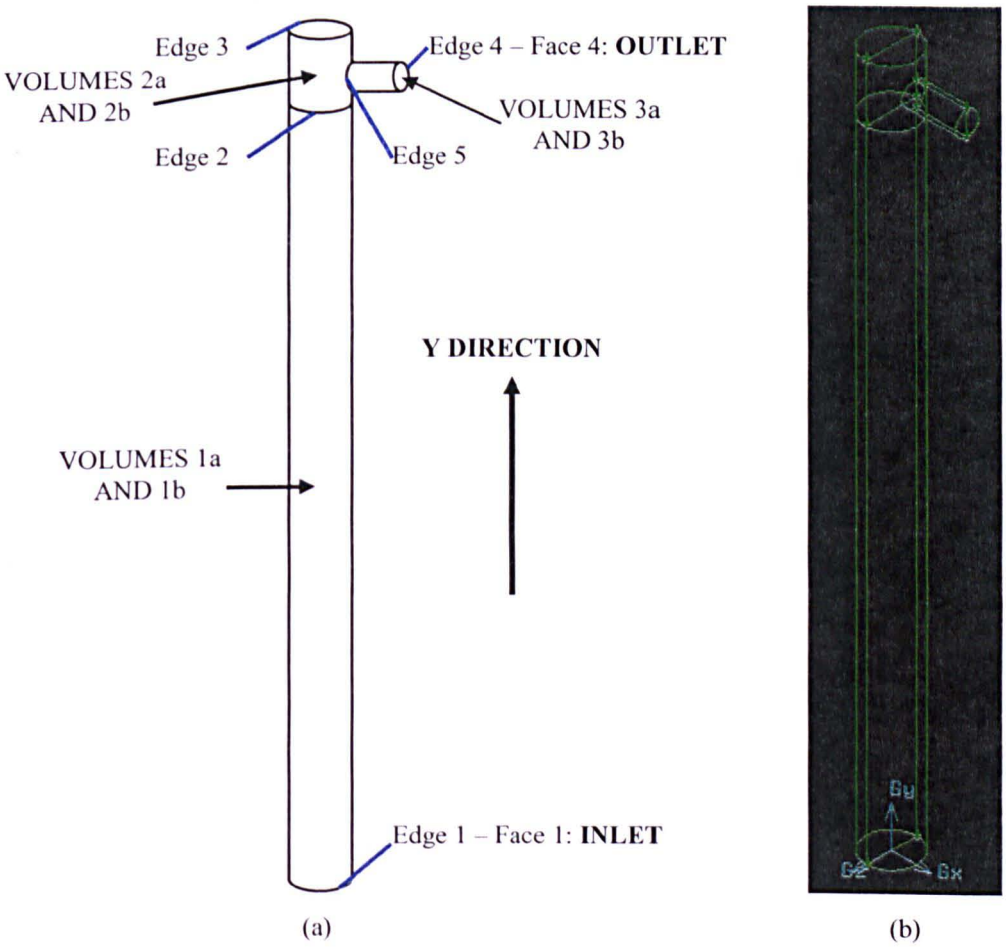
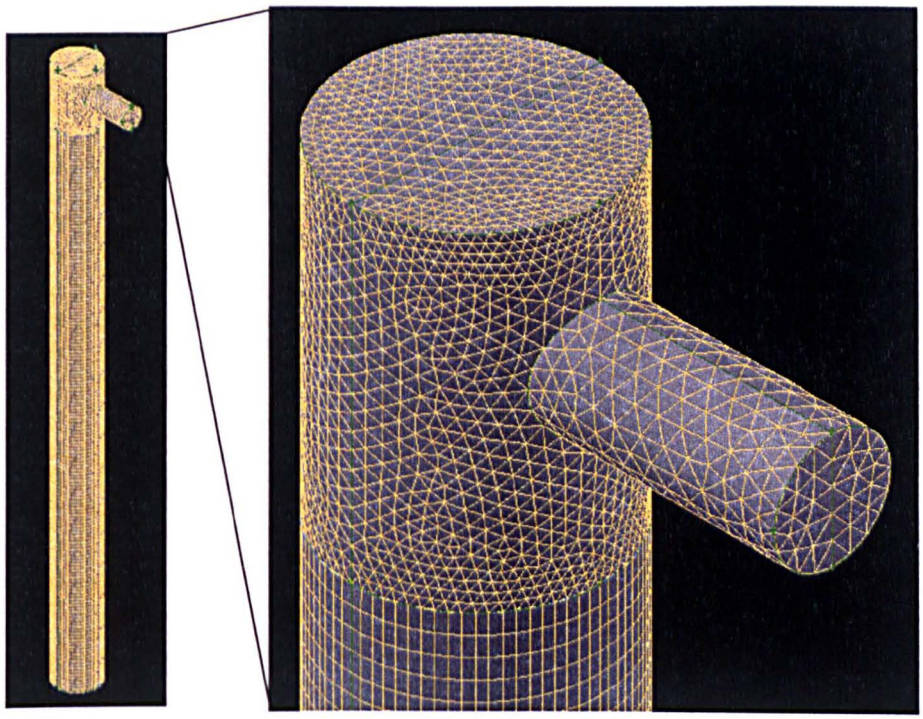


Figure 10.1: Laboratory-scale fluidised-bed geometries: (a) scaled schematic and (b) GAMBIT geometry.

The second phase was then completed, where Edges 1, 2 and 3 were meshed using an interval count of 80 (40 points per half) and Edge 4 was meshed using an interval count of 20 (10 points per half), as it was smaller. The faces using these were meshed using a Tri Element mesh, with an interval size spacing of 1, relative to the meshes on their respective edges. In order to mesh Volume 1, the length was first meshed, using an interval count of 145. Subsequently Volumes 1a and 1b were meshed using Hex/Wedge elements, with a spacing of 1 interval size, relative to the meshes on its length and Edges 1 and 2. The length of Volume 2 was meshed using an interval count of 10. Volumes 2a and 2b were then meshed using Tet/Hybrid elements, with a spacing of 1 interval size. The length of Volume 3 was first meshed using an interval count of 10 and then the volumes were meshed with a spacing of 1 interval size and Tet/Hybrid elements. There were approximately 142,000 elements in the entire mesh. Figure 10.2 shows the entire grid and a portion of the mesh geometry (Volumes 2a, 2b, 3a and 3b).



(a) (b)

Figure 10.2: GAMBIT geometries of the surface mesh of (a) the entire grid and (b) the top of the reactor.

Lastly, for the third phase, specific boundary types were specified, as outlined on Figure 10.1. Face 1, at the base of the reactor, at the boundary with the sand bed was designated the mass flow inlet (INLET) and the exhaust exit, Face 4, was assigned as the outflow (OUTLET). The rest remained as walls (WALL). This would later enable the various boundary conditions to be allocated to these different zones in FLUENT. The mesh was saved and exported as a mesh file (.msh) for subsequent use in FLUENT.

10.2.3 Comparing the Experimental and Modelled Results

10.2.3.1 Purpose, Objectives and Conditions of FLUENT Modelling

The primary purpose of modelling the combustion of these wastes was to compare the experimental data to the model results. The overall discrepancies between these would be able to give a good indication of the accuracy of the model. Once the optimum conditions had been determined, this would provide a good basis for further modelling, such as assessing the transport disengagement height (TDH). The stages outlined in Section 10.2.1.3 were completed. Since the meshed geometry had been created and exported from GAMBIT, it could then be read into FLUENT (using the 'FILE – READ – CASE' menu). The geometry was then scaled to SI units ('GRID – SCALE'), by using the unit conversion function – stating the units the grid was created in, in this case cm – and then scaling the geometry according to the calculated scale factor. Once scaled, the modelled geometry was thus 2.08 m high and 0.15 m wide, with a 0.15 m long exhaust pipe (diameter of 0.07 m), located 0.05 m from the top of the reactor. The mesh was then smoothed and swapped ('GRID – SMOOTH/SWAP'), and checked, as outlined in Figure 10.3, which summaries the meshed grid. This completes Stage 1 – establishing the meshed geometry and reading it into FLUENT.

```
Grid Check

  Domain Extents:
      x-coordinate: min (m) = -7.499999e-02, max (m) = 2.250000e-01
      y-coordinate: min (m) = -4.592274e-18, max (m) = 2.080000e+00
      z-coordinate: min (m) = -7.499999e-02, max (m) = 7.499999e-02
  Volume statistics:
      minimum volume (m3): 9.407072e-09
      maximum volume (m3): 1.030283e-06
        total volume (m3): 3.729087e-02
  Face area statistics:
      minimum face area (m2): 7.040969e-06
      maximum face area (m2): 2.276175e-04
  Checking number of nodes per cell.
  Checking number of faces per cell.
  Checking thread pointers.
  Checking number of cells per face.
  Checking face cells.
  Checking bridge faces.
  Checking right-handed cells.
  Checking face handedness.
  Checking face node order.
  Checking element type consistency.
  Checking boundary types.
  Checking face pairs.
  Checking periodic boundaries.
  Checking node count.
  Checking nosolve cell count.
  Checking nosolve face count.
  Checking face children.
  Checking cell children.
  Checking storage.
Done.
```

Figure 10.3: The results of the grid check in FLUENT.

Stage 2, as described above, makes use of the 'DEFINE' menu and the functions contained within. There are four sub-menus within this, of which the inputs are considered below:

1. 'DEFINE – MODELS':
    - 'Solver' - within this menu, a pressure-based solver was chosen (over density-based) and the implicit formulation (default) was kept. The default settings of 3D space and steady time were selected. Absolute velocity formulation was chosen and superficial velocity over physical velocity was used in the porous formulation. Lastly, the Green-Gauss cell-based gradient option was checked.
    - 'Multiphase' - the multiphase model remained off, the default setting.
    - 'Energy' - the energy equation was selected.
    - 'Viscous' - the standard k-epsilon (2-eqn) model was chosen, with the default model constants. Standard wall functions were selected for the near-wall treatment. There were no user-defined functions for turbulent viscosity or Prandtl Numbers selected.
    - 'Radiation' - the P1 radiation model was specified, yet the solar load model remained off.
    - 'Species ~ Transport and Reaction' - the species transport model was selected, using volumetric reactions. From the turbulence-chemistry interaction menu, finite-rate/eddy-dissipation was chosen. Within the mixture properties menu, propane-air-2step was selected as the mixture materials, resulting in 6 volumetric species, discussed further below. Within the options, diffusion energy source, full multi-component diffusion and thermal diffusion were selected. Inlet diffusion was only included for some scenarios, as specified later[1].
    - 'Discrete Phase' - these settings were left at their defaults.
    - 'Solidification and Melting' - these are not selected by default.

2. 'DEFINE – MATERIALS':
   - For the material type of 'mixture', the fluent materials were already propane-air-2step, as selected above, which meant N_2, CO, CO_2, O_2, C_3H_8 and water vapour were used in the reaction. This 2 step approach meant that CO was included in the species mixture, thus making the calculations more accurate, as CO was indeed present in the reactor during the experiments. The properties of the materials were not altered from their default settings.
3. 'DEFINE – OPERATING CONDITIONS':
   - The operating pressure was left at the default setting (101,325 Pa), as the fluidised-bed was not pressurised. The gravitational acceleration was set at 9.8 m/s^2 in the negative Y direction (according to Figure 10.1) for some simulations, as detailed later[2]. Within the Boussinesq parameters, the operating temperature was specified as 1141 K, considered in Table 10.1.
4. 'DEFINE – BOUNDARY CONDITIONS':
   - Boundary conditions were set for the INLET, OUTLET and WALL, specified in the GAMBIT geometry. The INLET (mass flow inlet) was set for momentum, thermal, radiation and species. Firstly, in the momentum tab, mass flow specification was selected as mass flowrate, calculated as 0.00681 kg/s, as detailed in Table 10.1. Within the direction specification, normal to boundary was chosen over defining the direction vector. Next, in turbulence specification, the turbulence intensity was set at 3 % and the hydraulic diameter set at 0.15 m (the diameter of the reactor cylinder). Under the thermal tab, the total temperature was specified at 1141 K, shown in Table 10.1. Within the radiation tab, the external black body temperature method was left at the default of boundary temperature, with a constant internal emissivity and flow rate weighting both of 1. Lastly, under the species tab, the mass fractions of O_2 and C_3H_8 were outlined. Fractions for CO_2 and water vapour (H_2O) could also be specified here, detailed in Table 10.1.
   - For the OUTLET (outflow), the external black body temperature was set at the default boundary temperature, with a constant internal emissivity and flow rate weighting both of 1.
   - The WALL was set for momentum and thermal factors. Under the momentum tab, the wall motion was left as stationary, with no slip under the shear conditions. Wall roughness was left at the default. Under the thermal tab, conditions were set for the wall temperature; this changed for each case modelled, as specified below[3], with a constant internal emissivity of 1. The wall material was set to aluminium.

Within the above summary of the modelling set-up, various quantities were left undefined, as these changed between the cases modelled. In Table 10.1, these parameters are outlined for each case, which were designed to compare the modelled and experimental data. Eight simulations were completed to find an optimum model scenario that best represented experimental Case 1; this had a primary air flowrate of 415 kg/m^2hr and a pellet feedrate of 3.52 kg/hr, resulting in an air ratio of 2.13. The input data for the species mass fractions of the reactants and products were therefore calculated based on these values and those for the exhaust gas concentrations.

Stage 3 used the 'SOLVE' menu, where the parameters were set for the problem. Firstly, the equations that needed to be solved were selected, in this case, flow, turbulence, energy, P1 and the material species (C_3H_8, O_2, CO_2, CO and H_2O). Simple pressure-velocity coupling was left at the default setting, as were the under-relaxation factors. Lastly, the discretization parameters were chosen, in terms of pressure (standard), momentum (first order upwind), turbulent kinetic energy (first order upwind), turbulent dissipation rate (first order upwind), the material species selected (C_3H_8, O_2, CO_2, CO and H_2O, all first

order upwind) and the energy (first order upwind). For Stage 4, the solution was initialized, using 'SOLVE – INITIALIZE – INITIALIZE'. Here, it was specified that the data should be computed from all zones and the other settings left at their defaults the case was then iterated, using 20,000 iterations, until the convergence criteria were satisfied.

INPUT DATA		MODEL CASE							
		1	2	3	4	5	6	7	8
Operating Temperature (K)		1141	1141	1141	1141	1141	1141	1141	1141
Mass Flowrate (kg/s)		0.00681	0.00681	0.00681	0.00681	0.00681	0.00681	0.00681	0.00681
Total Inlet Temperature (K)		1141	1141	1141	1141	1141	1141	1141	1141
Species Mass Flow Fractions at Inlet	C_3H_8	0.00016	0.00016	0.00016	0.00016	0.00016	0.00016	0.00016	0.00016
	O_2	0.04124	0.04124	0.04124	0.04124	0.04124	0.04124	0.04124	0.04124
	CO_2	0.24267	0.24267	0.24267	0.24267	0.24267	0.24267	0.24267	0.24267
	H_2O	0.04353	0.04353	0.04353	0.04353	0.04353	0.04353	0.04353	0.04353
[1]**Inlet Diffusion**		yes	yes	yes	yes	yes	yes	no	no
[2]**Gravity**		yes	no	yes	yes	yes	yes	no	yes
[3]**Wall Temperature (K)**		323	323	373	423	448	473	323	323

Table 10.1: Input parameters for the operating and boundary conditions for the eight different model cases for the scenarios to imitate the experimental conditions.

10.2.3.2 Analysis of the Modelled Data

The experimentally-determined gas concentrations and temperatures for experimental Case 1 were compared to the 8 model cases. The O_2, CO and CO_2 concentrations in the exhaust gas were compared with the model predictions for these at the outlet. The temperatures were compared for the 6 thermocouples just above the bed and in the freeboard of the reactor, the locations of which (T3 to T8) are given in Table 10.2 for both the experimental and model cases. The locations of these thermocouples in the fluidised-bed reactor were shown in Figure 9.1, where the tips were located in the centre. As seen, thermocouples T1 and T2 were located within the sand bed and thus were not modelled here.

THERMOCOUPLE	EXPERIMENTAL	MODEL
T3	y=0.31 m	y=0.09 m
T4	y=0.42 m	y=0.20 m
T5	y=0.56 m	y=0.34 m
T6	y=0.76 m	y=0.54 m
T7	y=1.54 m	y=1.32 m
T8	y=1.74 m	y=1.52 m

Table 10.2: Locations of the thermocouples in the experimental and modelling setup. The locations are equivalent in each case and are at the centre of the reactor.

10.2.3.3 Results of FLUENT Modelling Compared to Experimental Data

Using the data gained from the combustion of the SMC-coal tailing pellets (Experimental Case 1), it was attempted to run the FLUENT model under the same conditions to simulate similar results and thus evaluate the validity and accuracy of the model. As the gas concentrations at the outlet and the temperatures throughout the reactor were monitored during the experiments and these could also be modelled, comparisons between these were made (Table 10.3). Eight scenarios were modelled to see

which input parameters were most suitable for imitating the experimental conditions and results, where the wall temperature, gravity and inlet diffusion were altered between the cases (Table 10.1).

PARAMETER		EXPERIMENTAL CASE 1	MODEL CASE 1	2	3	4	5	6	7	8
Average Gas Concentration (%)	CO_2	14.6	16.6	16.6	16.6	16.6	16.6	16.6	16.6	16.6
	O_2	4.0	3.8	3.8	3.8	3.9	3.8	3.8	3.8	3.8
	CO	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Average Temperature (°C)	T3	872	868	868	868	868	868	868	868	868
	T4	868	868	868	868	868	868	868	868	868
	T5	823	867	867	867	867	867	867	867	867
	T6	803	861	866	864	865	865	866	866	861
	T7	505	396	727	437	478	497	516	727	396
	T8	464	335	616	384	428	449	470	616	339

Table 10.3: Comparison of the experimental data for gas concentrations at the outlet and temperatures throughout the freeboard to the eight different model scenarios.

The gas concentrations were similar to those monitored experimentally and there was hardly any variation in the data between the cases. As there was excess O_2 in the system, the model assumed that all CO would be further oxidised to CO_2, thus no CO was present in the model results. In reality, the mixing in the system was poor and thus some CO was released without further oxidation, as it was probably in a zone with a fairly low amount of excess oxygen, known as a dead zone. This also accounts for the larger quantity of CO_2 and the smaller amount of O_2 in the model results. The combustion efficiency for all the modelled cases would be 100 %, whereas the experimental data shows the presence of the CO reduced this to ~95 %. The outcome for all cases was extremely similar, despite the variance in input conditions.

The temperatures throughout the reactor are also shown in Table 10.3 and as can be seen, there was much more variation in these results for the different cases, compared to the gas concentration data, as the wall temperature, along with inlet diffusion and gravity, changed between the different scenarios. The experimentally-recorded temperature for T3 was high, 872 °C, as the majority of combustion would be taking place in and just above the bed. The model suggested that all fuel (propane) would be consumed within the bottom third of the reactor, thus the model also showed the highest temperatures in this area (T3-T5), as shown in Figure 10.4. This was also where the fastest gas velocities were predicted to be, as seen in Figure 10.5. The temperatures predicted in this region were the same for each model scenario. The temperatures recorded at the top of the freeboard (T7 and T8) were much lower, which was also reflected in the model, although there was much disparity between the different cases. Cases 5 and 6 offer the best results regarding the temperatures at these locations. For the remaining thermocouples (T5 and T6), the predicted temperatures for all eight scenarios were much higher (50-60 °C) than those determined experimentally, regardless of the input parameters.

The results for Model Cases 5 and 6 appeared to best represent the experimental data and this gives a good basis for the further modelling cases, as these were the most accurate for temperature predictions, each having an overall percentage error of just 3 % (the difference between the experimental data and the

predicted results from the model). Modelled Cases 2 and 7 were the least accurate, each with overall errors of over 15 % for temperature predictions. All simulations produced extremely similar results for the gas concentrations at the outlet and corresponded well to the experimental data. Based on the input parameters for these two cases (Model Cases 5 and 6), it shows that the wall temperature should be set to around 448-473 K (175-200 °C), with inlet diffusion on. Gravity should also be on to best imitate reality, set at 9.8 m/s^2 in the negative Y direction.

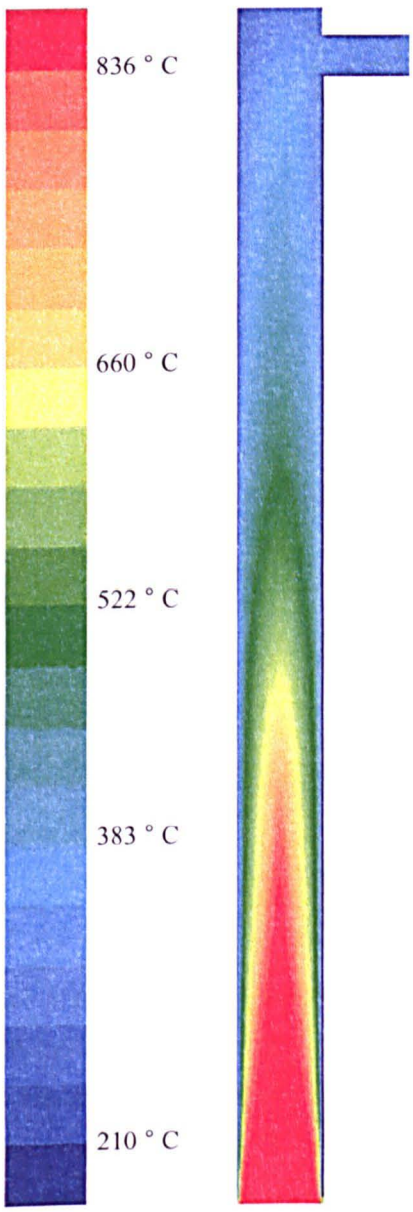


Figure 10.4: Temperature contours at the centre surface of the reactor for Model Case 5.

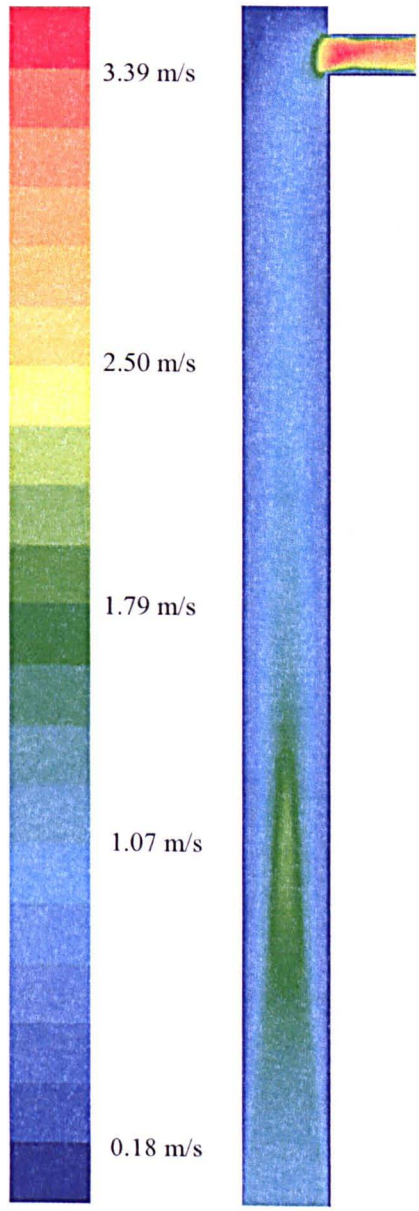


Figure 10.5: Velocity magnitude contours for the centre surface for Model Case 5.

Velocity magnitude contours for the centre surface are shown in Figure 10.5 for Model Case 5. Velocity measurements were not conducted during the experiments, thus direct comparisons cannot be made. The model predicts that the velocity in the main body of the reactor is quite fast – moving upwards (in the positive Y direction, according to the vectors) at between 1.0 m/s and 2.0 m/s. The fastest gas flow in the main part of the reactor is towards the bottom half (pale yellow-green colour), which corresponds well

with the top of the hottest section, when compared to Figure 10.4 (red section). Overall, the most rapid gas movement is thought to be at the exhaust pipe, where gas speeds exceed 3.0 m/s. This is due to the smaller pipe diameter of the exhaust compared to the main reactor body. The velocity vectors at this location were thus perpendicular to those in the main reactor body – in the positive X direction (Figure 10.6). The effect of the boundary layer on the velocity magnitude contours is quite clear; the velocities at the wall are significantly lower than those seen at the centre, due to the wall roughness equations included in the model, which cause friction and therefore a deceleration of the gas.

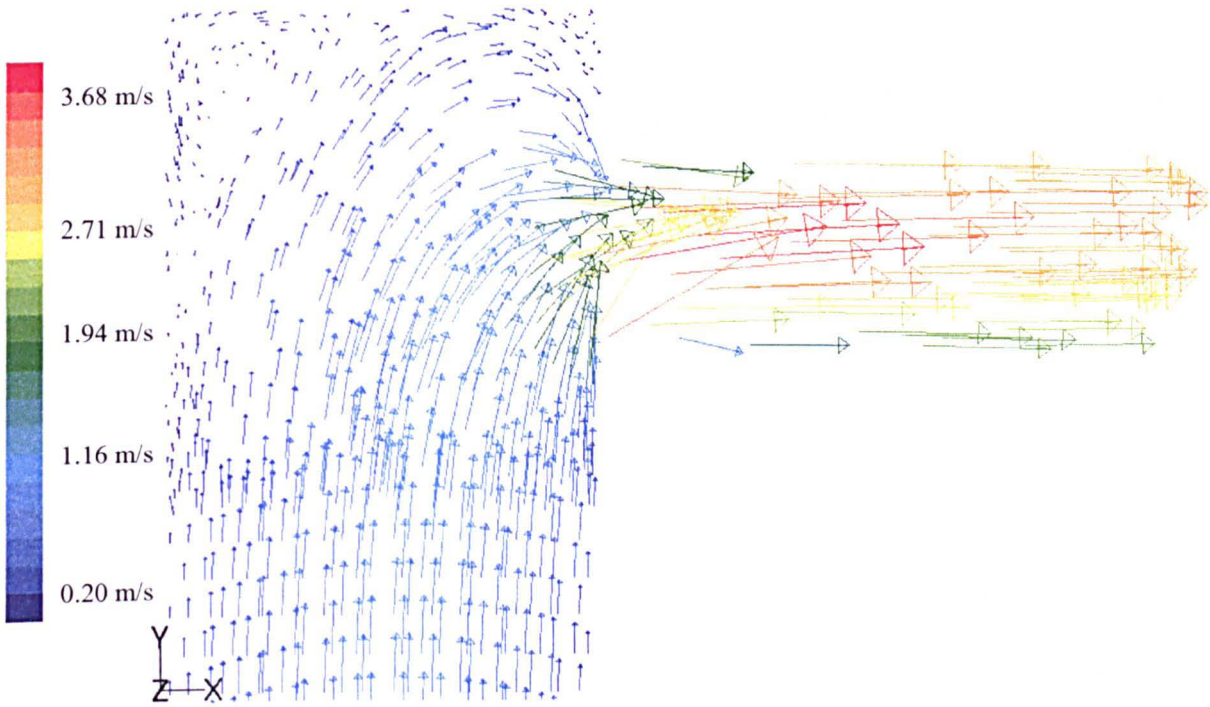


Figure 10.6: Velocity vectors, coloured by magnitude, at the top of the centre surface for Model Case 5.

10.2.4 Particle Elutriation and Entrainment

10.2.4.1 Purpose, Objectives and Conditions of FLUENT Modelling

As the most appropriate conditions for replicating the experimental results were determined, particles could subsequently be added at the base of the reactor. This enabled the assessment of sand and flyash elutriation, based on the terminal velocity of the particles. From this, the TDH, a concept introduced in Section 4.3.2, was established. By tracking particles at suitable gas velocities (based on those computed above), it could be seen if sufficient freeboard height was provided and whether particles, particularly the flyash, would escape with the flue gases. It was thought that sand particles would eventually fall back to the bed, whereas flyash would leave the combustor at the exit modelled, as with the experimental cases.

The same GAMBIT geometry was used here as above and the input conditions were those for Model Case 5 (Table 10.1). Particle elutriation was modelled by using addition functions within the 'DEFINE' menu. In 'DEFINE – MODELS – DISCRETE PHASE' (or 'DEFINE – INJECTIONS'), the parameters for the injections of particles can be created or set. Using a surface injection type, the inlet could be specified as the surface from which the particles were released, using an inert particle type. Only the

point properties were modified; all other options were left at their default settings. Three cases were modelled; the first two (Cases A and B) concerned sand particles, where values were set for diameter (0.00085 m) and temperature (1141 K). A flowrate of 0.00058969 kg/s was used, based on the fact that one sand particle entered the freeboard from the bed from each of the 834 grid cells at the inlet and the sand had a density of 2200 kg/m^3. Velocity in the X, Y and Z directions were set, which was the variable manipulated between the cases. The velocities in the X and Z directions were 0 m/s, whereas the Y velocity (parallel with the walls) was set in the positive direction at 1.0 m/s for Case A and 2.0 m/s for Case B. These velocity magnitudes were based on the results shown in Figure 10.5. Values were only set for the Y velocity in these cases, as the primary air which enters from the base of the reactor would be mainly flowing in this direction, due to the angle of the standpipe nozzles on the distributor plate. Case C concerned flyash elutriation and utilised the same method as above. Here, the data inputs were a particle diameter of 0.00003 m and a mass flowrate of 0.00000000617 kg/s, based on a density of 523.45 kg/m^3. The X and Z velocities were set at 0 m/s, whereas the Y velocity was set at 1.0 m/s, as for Case A.

10.2.4.2 Results of Modelling Particle Elutriation and Entrainment

Particles of appropriate size and density were injected into the modelled combustion chamber, where the conditions were those that most closely represented the experimental data. Figures 10.7a and 10.7b show the heights the entrained sand particles from the fluidised-bed reached for different gas velocities. The heights reached were generally the same for a specific velocity and there was little variance. Particle speeds, however, did vary significantly along their trajectories. When the particles initially elutriated, their speeds were computed to be quite fast, similar to those of the surrounding gases. After the particles reached their maximum height, at which point the velocities are significantly lower than when they were first entrained, they start to return to the bed after having lost even more momentum. This is principally due to the resistance of the primary air flowing in the opposite direction to the falling particles. The TDH in both cases was thought to be small in comparison to the freeboard height (above the bubbling sand bed). For a gas speed of 1.0 m/s, which most closely resembled those modelled at this location within the reactor (Figure 10.5), the TDH was approximately 0.07 m above the surface of the bed. At faster velocity magnitudes, the maximum height the particles were entrained to was only 0.22 m above the bed. Even at these velocities, the upward force of the gas was not sufficient to keep the dense particles entrained and thus enough freeboard height was provided within the reactor to prevent bed particles escaping with the exhaust gases. This was confirmed by the experimental data, as sand bed particles were not collected with the flyash in the cyclone, situated at the end of the exhaust pipe, but remained in the bed.

As shown from Figure 10.7c, however, a gas velocity of 1.0 m/s was adequate to keep the smaller, lighter flyash particles entrained, which were then removed from the reactor. As the experimental results demonstrated, such particles were indeed collected in the cyclone and did not remain in the bed. The swirling motion exhibited by these particles near the combustor exit, shown in Figure 10.8, is due to their tangential momentum as they continue to move through the system from the freeboard to exit.

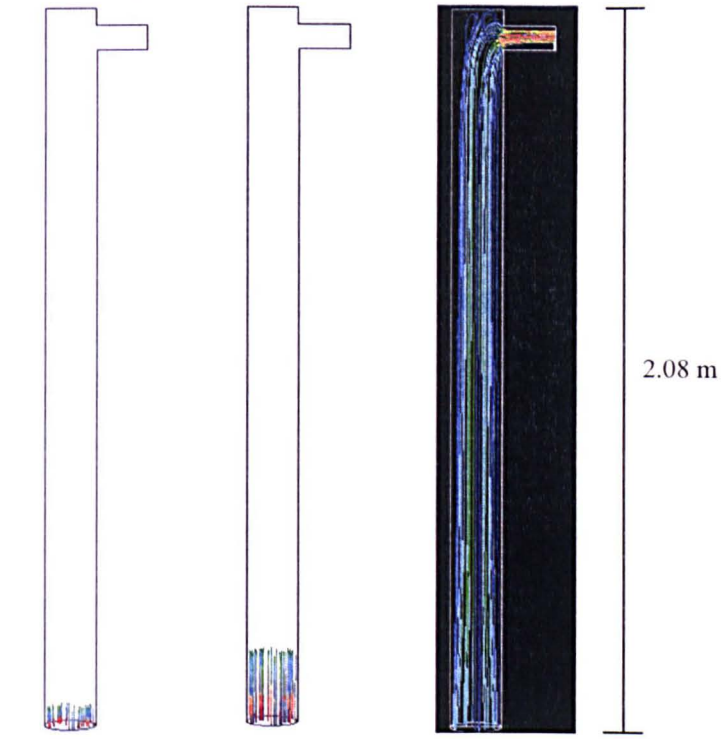


Figure 10.7: Particle tracks for: (a) Case A – sand elutriation, where Y=1.0 m/s, (b) Case B – sand elutriation, where Y=2.0 m/s, and (c) Case C – flyash particulate elutriation, where Y=1.0 m/s.

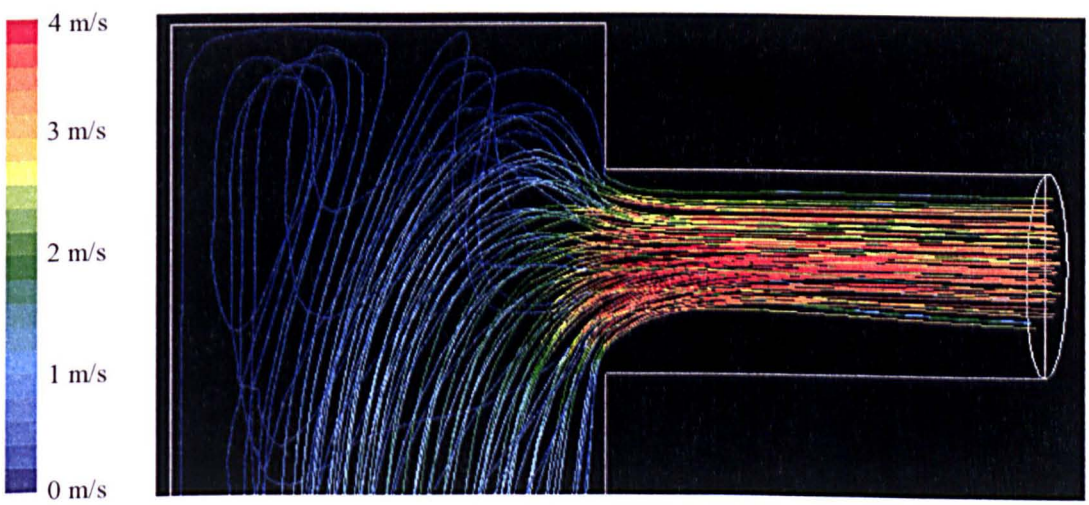


Figure 10.8: Particle tracks, showing their speeds and trajectories, for flyash particulates in the exhaust exit.

10.3 HEAT AND POWER GENERATION: INDUSTRIAL APPLICATIONS

The generation of heat and power from these wastes can be accomplished by combusting the fuels and utilising a combination of a boiler and steam turbine to recover energy. Through the previous experimental work completed herein, such as the determination of the fuel properties, mass and energy balances can be completed for the combustion phase, boiler and dryer. Additional data is required, such as input parameters regarding the process, assumptions concerning the furnace, boiler and dryer, and a range of physical properties of the steam. From this, the overall electrical output for this process can be estimated; four cases were compared, where the fuel throughput was varied.

10.3.1 Furnace, Boiler, Dryer and Steam Turbine

The theoretical set-up used for this simulation of electrical output from the combustion of these wastes consisted of a furnace, a boiler, a steam turbine for energy recovery and a direct dryer to dry the initial materials. The furnace is used to combust the fuel and produce heated gases, which are then used to create steam, which passes through the boiler system, as shown in Figure 10.9. The steam turbine is then used to generate the power, from which the electrical output can be computed. The dryer utilises any excess heat generated from the combustion process to dry the input materials to appropriate moisture levels, as the moisture content on an 'as received' basis was extremely high, for both the SMC and coal tailings. This use of waste heat to dry the input fuel was considered by Maher, *et al.* (2000), as outlined in Section 2.4.3.1. In order to recover as much energy as possible from such a process, it is vital that the moisture content of the fuel is low, especially since the CV of the initial materials are not very high.

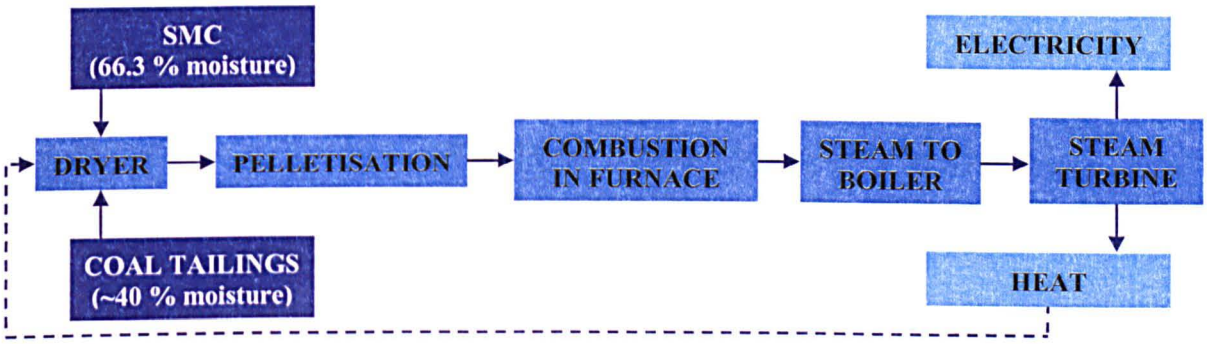


Figure 10.9: Flow diagram of the inputs and outputs, as well as the processes and equipment utilised during the formation of the SMC-coal tailing pellets and the energy recovery process.

Any additional heat not used for drying could be utilised to produce a cheap, sustainable source of heating for the facility, if it located at or in close proximity to it. Mushroom cultivation uses highly controlled temperatures, thus the low grade heat could be used for this purpose. Alternatively, it could also be used during the 'cooking-out' process, described in Section 2.4.1. If the heat recovery system is not close enough to provide heating to the farm, district heating could be made available for local populations.

10.3.2 Governing Equations

Based on the material and pellet properties and the amount of fuel utilised, along with details concerning the furnace, boiler and dryer, mass and energy balances were computed for each stage, from which the overall electrical output was determined. Firstly, the mass balances for the various stages were computed. From determining a fuel mass flowrate into the furnace, which is varied here between the four cases compared, the mass of air required was computed. This was dependent on the combustion stoichiometry of the fuel and the excess air ratio needed, which were kept constant. As the inputs into the system were known (i.e. the mass of the fuel and the air), the outputs (the mass of the ash and the mass and composition of the exhaust gases) were ascertained. The energy balance for the furnace was thus based on the physical, chemical and thermodynamic properties of the fuel, air, exhaust gases and ash, and the heat losses during combustion, which include such losses as those to the wall and in the ash, as well as

those from the release of unburned material. The temperature and pressure of the steam generated during combustion was used to calculate the mass and energy balances for the boiler. The energy balance for this stage was completed in a similar manner to that of the furnace, where the same data was utilised. Lastly, a steam mass balance was completed from the temperatures and enthalpies of the water going into the boiler and that of the steam output, from which the mass of steam generated was calculated. For the steam turbine, an overall process efficiency of 18.6 %, a function of the steam temperature, was assumed. Based on these data, the overall power generation was determined – consisting of both the electrical output in MWe and the energy that goes to the condenser (MWth).

10.3.3 Input Data and Physical Properties

The input data required for this purpose consisted of the properties of the SMC and SMC-coal tailing pellets, which had been previously determined. The process input parameters regarding the process were broken down into the following: fuel throughput, air requirements and fuel properties going to the furnace, and the properties and operating conditions of the furnace, boiler and dryer. The input values used are given in Table 10.4, showing the data for the four different cases compared.

PROCESS INPUT PARAMETERS		DATA VALUE			
		Case 1	**Case 2**	**Case 3**	**Case 4**
Pellet Throughput	Fuel	SMC	SMC-CT	SMC-CT	SMC-CT
	kg/s	0.32	0.63	6.34	12.68
	ton/hr	1.14	2.28	22.83	45.66
	ton/day	27.40	54.79	547.95	1095.89
	ton/a	10,000	20,000	200,000	400,000
Air Requirements	Pressure (bar)	1.0	1.0	1.0	1.0
	Temp. (K)	298.15	298.15	298.15	298.15
	N_2 in air (per mole O_2)	3.76	3.76	3.76	3.76
	Air Temp. (K)	288.15	288.15	288.15	288.15
	Density (kg/m^3)	1.21	1.21	1.21	1.21
Fuel	Wet Input (kg/s)	0.32	0.63	6.34	12.68
	Dry Input (% of Wet Input)	100	100	100	100
	Moisture of Fuel (%)	10.50	10.50	10.50	10.50
Furnace	Excess Air Ratio	0.40	0.40	0.40	0.40
	Heat Loss (% of HHV)	5.00	5.00	5.00	5.00
	Fuel Temp. (K)	288.15	288.15	288.15	288.15
Boiler	Water Temp. In (K)	288.15	288.15	288.15	288.15
	Steam Pressure (bar)	6.00	6.00	6.00	6.00
	Steam Temp. Out (K)	533.15	533.15	533.15	533.15
Dryer	Steam Temp. Out (K)	423.15	423.15	423.15	423.15
	Heat Loss (%)	5.00	5.00	5.00	5.00
	Temp. of Fuel In (K)	288.15	288.15	288.15	288.15
	Temp. of Fuel Out (K)	336.99	337.15	337.15	337.15
	Target Fuel Moisture (%)	10.50	10.50	10.50	10.50
	Flue Gas Temp. Difference (K)	10.00	10.00	10.00	10.00

Table 10.4: Process input parameters for the estimation of the electrical output from the industrial-scale combustion of SMC-coal tailing pellets.

As shown above, the cases compared various fuel throughputs. Case 1 was based on a small-scale operation, where 10,000 t/a of unpelletised SMC could be utilised, for example the amount of waste

generated from the farm in Whitley, Yorkshire, UK that was the source of SMC for this investigation, considered in Section 2.4.2. This would imitate the energy that could be generated if this specific farm introduced an on-site EfW incinerator. For Case 2, the SMC is combined with 10,000 t of coal tailings from nearby Maltby colliery, the source of this waste for this investigation, discussed in Chapter 2. As described in Section 2.4.2, Williams, *et al.* (2001a) assumed that 100,000 t of the 190,000 t/a of SMC produced in the Irish boarder counties would be available for energy recovery. Case 3 therefore looked at a medium-sized central energy recovery facility in this area, where the SMC combines with equal amounts of coal tailings. This size of incinerator is similar to the Sheffield energy recovery facility, described in Section 2.2.1.3, which currently utilises 28 t of waste an hour, dealing with approximately 225,000 t of local MSW each year. This generates up to 19 MW of electricity and up to 60 MW of heat (Veolia Environmental Services, 2007). Finally, Case 4 simulates a larger, centralised EfW facility, where all 200,000 t of SMC produced annually in the UK is combined with 200,000 t of coal tailings.

The steam temperature out of the boiler had to be above the boiling point (saturation temperature) of water at the pressure stated, in this case, 6 bar (i.e. above 158.8 °C or 431.95 K), prior to superheating to around 400 °C for energy generation. The fuel properties were required on an air dried basis; the 10.5 % moisture content is the optimum for the pelletisation of these materials, determined by the tests outlined in Section 7.5.1. Although three cases compared various pellet throughputs, their properties remained the same for each case. Data for the CV and the ultimate and proximate analyses, as determined in Section 6.3.2, were used as input data; Table 10.5 shows these for the SMC used in Case 1 and the pellets used in Cases 2 through 4. The physical properties that were required to complete these calculations included the molecular weights of the elements in the fuel composition (those in Table 10.5) and those of the gaseous species in the exhaust (CO_2, H_2O, O_2 and N_2). Thermodynamic properties of these gases and the fuel were needed and data regarding the steam vapour pressure and the latent heat of water were also used.

PROPERTY	SMC	SMC-COAL TAILINGS
Ash (%)	35.82	39.48
C (%)	35.25	41.56
H (%)	3.47	3.19
N (%)	2.50	1.76
S (%)	2.79	2.09
Cl (%)	0.55	0.27
O (%)	19.62	11.65
HHV (MJ/kg)	13.76	16.81
As Received Moisture (%)	66.27	53.14
Air Dried Bulk Density (kg/m^3)	387	496

Table 10.5: Input data for the estimation of the electrical output from the combustion of these wastes.

10.3.4 Results for Mass and Energy Balances and Electrical Output

The results from these calculations can be seen in Table 10.6, which shows the mass and energy balances for the various stages comparing the different cases. This also gives the steam properties and the overall electrical output that could be generated from the combustion of different amounts of these wastes.

FURNACE		CASE 1	CASE 2	CASE 3	CASE 4
Mass Balance (ton/hr)	Fuel In	0.43	1.20	11.95	23.91
	Air In	2.36	8.01	80.09	160.18
	Gas Out	2.63	8.74	87.38	174.76
	Ash Out	0.16	0.47	4.66	9.33
At Furnace Exit (ton/hr)	CO_2	0.50	1.63	16.29	32.58
	H_2O	0.17	0.43	4.33	8.65
	O_2	0.16	0.53	5.33	10.66
	N_2	1.81	6.14	61.43	122.86
	Total Mass Out (Ash + Gas)	2.79	9.20	92.04	184.09
Energy Balance for Furnace Exit (MJ/s)	Combustion	1.29	4.47	44.68	89.37
	Fuel In	0.00	-0.01	-0.08	-0.17
	Gas In	-0.01	-0.02	-0.23	-0.46
	Gas Out	1.11	3.88	38.82	77.63
	Ash Out	0.11	0.33	3.32	6.64
	Gas Temp. (K)	1583.9	1690.9	1690.9	1690.9
BOILER					
Gas Out	Temp. (K)	1037.50	678.02	677.78	677.78
	Dry Mass Flowrate (kg/s)	0.76	2.43	24.27	48.54
Energy Balance for Boiler (MJ/s)	Combustion	1.36	4.70	47.04	94.07
	Fuel In	0.00	-0.01	-0.08	-0.17
	Gas In	-0.01	-0.02	-0.23	-0.46
	Gas Out	0.63	1.02	10.18	20.36
	Ash Out	0.06	0.09	0.91	1.81
	Loss/Other	0.07	0.24	2.35	4.70
	Difference	0.59	3.33	33.28	66.57
Steam Mass Flow and Temp.	Temp. Water In (K)	306.05	306.05	306.05	306.05
	Temp. Steam Out (K)	533.15	533.15	533.15	533.15
	Enthalpy Water In (MJ/kg)	0.13	0.13	0.13	0.13
	Enthalpy Steam Out (MJ/kg)	2.98	2.98	2.98	2.98
	Mass of Steam (ton/hr)	0.75	4.21	42.21	84.24
	Mass of Steam/Mass of Fuel (kg/kg)	1.75	3.52	3.52	3.52
DRYER					
Moisture Evaporated (% of Fuel In)		62.31	47.64	47.64	47.64
Combustion Gas Saturation Temp. At Dryer Exit (K)		348.28	336.99	336.99	336.99
Mass Balance (kg/s)	Fuel In	0.32	0.63	6.34	12.68
	Fuel Out	0.12	0.33	3.32	6.64
	Mass of Flue Gas In	0.73	2.43	24.27	48.54
	Mass of Flue Gas Out	0.93	2.73	27.29	54.59
Energy Balance (MJ/s)	Energy in Fuel In	-0.01	-0.02	-0.21	-0.42
	Energy in Flue Gas In	0.63	1.02	10.18	20.36
	Energy in Fuel Out	0.06	0.08	0.82	1.63
	Energy in Flue Gas Out	0.07	0.15	1.55	3.10
	Heat to Evaporate Water	0.46	0.71	7.10	14.19
	Heat Loss	0.03	0.05	0.51	1.02
Flue Gas Temp. (K)	Flue Gas Temp. In	1037.50	678.02	677.78	677.78
	Flue Gas Temp. Out	358.28	346.99	346.99	346.99
STEAM TURBINE					
Steam Properties	Inlet Pressure (MPa)	0.60	0.60	0.60	0.60
	Inlet Temperature (K)	533.15	533.15	533.15	533.15
	Outlet Pressure (MPa)	0.01	0.01	0.01	0.01
	Outlet Temperature (K)	305.15	305.15	305.15	305.15
	Steam Flowrate (ton/hr)	4.00	4.00	4.00	4.00
Electricity Generation	Electricity Output (MWe)	0.09	0.53	5.27	10.53
	Energy to Condenser (MWth)	0.50	2.80	28.02	56.04

Table 10.6: Results of the calculations for the furnace, boiler and dryer operation and electricity generation.

These four cases compared the use of the SMC alone with various throughputs of the SMC-coal tailing pellets. Case 1 had the lowest annual fuel feedrate; the steam turbine is thought to have an efficiency of 18.60 %, which when used with this SMC throughput led to an electrical output of around 0.09 MWe. This is quite low, primarily as this had the lowest fuel CV (HHV), as there were no higher CV coal tailings to improve the overall energy content of the fuel input. The unpelletised SMC also had a notably lower bulk density. This 0.09 MWe is the amount of energy that is likely to be generated if a single mushroom farm utilised only its own waste to produce energy, such as Monaghan Mushrooms in Whitley. By comparison, Case 2 shows the benefits of the addition of coal tailings and their superior CV, as well as the advantage of pelletising the wastes to increase the bulk density (as shown in Table 10.5). This case included 10,000 t/a of coal tailings in addition to the 10,000 t/a of SMC as utilised in Case 1 and a significantly better performance can be noted, where over 0.5 MWe could be generated. This energy could also be generated on the mushroom farm in Whitley if they combined their waste with the same amount of coal tailings from the nearby Maltby Colliery.

Case 3 was to simulate a dramatic increase in the scale of the energy recovery facility. Using a total of 200,000 t/a of the combined, pelletised fuels, for example in a medium-sized EfW facility similar to that in Sheffield, described above, approximately 5 MWe could be produced, in addition to 28 MWth. This is considerably less than the 19 MW of energy generated from MSW in Sheffield, even though the CVs of the fuels are likely to be similar; this is most likely due to the high moisture content of the materials here, which required much drying prior to their combustion. A low steam temperature was thus assumed. Approximately half of the amount of heat would be generated from SMC-coal tailing pellet combustion in this set-up, compared to that of the MSW. Lastly, using the maximum pellet feedrate of 400,000 t/a, in excess of 10 MWe could be produced, for instance in a centralised facility where all available SMC in the UK was exploited. This would also generate substantial amounts of thermal energy, for subsequent use. This would however result in the formation of significant quantities of ash (9.33 t/hr), which would require disposal or a market outlet for its use as an activator for PFA. The transport costs involved with this operation however are likely to be vast, as considered further consequently.

10.4 COMPLYING WITH LEGISLATION

The Waste Incineration Directive, described in Section 2.3.3, concerns the environmental implications of waste incineration throughout the EC. As both SMC and coal tailings are classified as wastes, even though they are used as fuels in this application, their combustion must conform to the emission limits outlined in this directive (Table 2.6). The fluidised-bed combustion tests of these fuels, reported in Chapter 9, monitored many of the emissions delineated in the WID criteria, thus comparisons can be made to determine the amount and type of gas cleaning that would be required. WID outlines emissions limit data for both gaseous and solid-phase pollutants. Here, CO, acid gases – NOx (NO and NO_2), SOx and HCl – and particulates were measured and can be contrasted accordingly. The implications of these pollutants on human health and on the environment were considered throughout Section 3.4.

CO was monitored for all tests and can be compared to the limits outlined in Table 2.6, which states that the maximum daily concentration should be 50 mg/m^3, with a half-hourly maximum of 150 mg/m^3 (DEFRA, 2006a). The average concentration in the exhaust for all tests was 1.08 %. The maximum was 2.47 %, recorded for the test where the air ratio was lowest. Accordingly, the lowest (0.10 %) was noted for the highest air ratio. Even this low concentration would be likely to exceed the regulation for this species, though this could be greatly reduced by optimising the combustion parameters on an industrial-scale and would therefore be expected to meet WID guidelines. Although optimum operating conditions were determined for the reactor employed, higher combustion efficiencies could have been achieved through converting more CO to CO_2, by way of modifying the experimental set-up, as previously discussed, such as scaling-up the reactor, including an after burner or the addition of staged secondary air.

The acid gas emission concentrations that were monitored are outlined in Table 10.7 below, along with the criteria for WID. Also included in this table are the relevant concentrations of N, S and Cl in the flyash samples. Previous studies indicated that the combustion of these fuels would not lead to high concentrations of NOx, SOx or HCl, although this does not mean that they would necessarily comply with emissions regulations without some form of gas cleaning (Williams, 2001; Williams, *et al.*, 2001a; Chugh and Patwardhan, 2004). As can be seen, NOx species concentrations were generally low, although some peaks were noted that were greatly above the average. Despite these significantly higher concentrations for short durations at various stages in some tests, both the average and maximum levels monitored were appreciably below the daily limits delineated in this directive. As such, expensive gas cleaning mechanisms, for instance SNCR or SCR, to remove NOx compounds are unlikely to be required, although their inclusion would obviously further minimise the negative environmental impacts of the release of such species. As the nitrogen was not found to be concentrated in the ash, N_2O is likely to have formed, as previously discussed. This may necessitate the inclusion of removal techniques into the gas cleaning phase to avoid the unwanted environmental effects of releasing this to the atmosphere, such as increasing atmospheric greenhouse gas concentrations.

EMISSIONS FROM EXPERIMENTS	NOx	SOx	HCl
Range	2.1-58.4 ppm	2.35-41.69 ppm	0.88-16.88 ppm
Average	10-20 ppm	12 ppm	5.3 ppm
Maximum	~91 mg/m^3	~123 mg/m^3	~25 mg/m^3
Daily WID Limits	200-400 mg/m^3 ~257 ppm	50 mg/m^3 ~19 ppm	10 mg/m^3 ~6.7 ppm
Ash	N not abundant in the ash, 0.29 % – N_2O?	majority of S found in the ash: 15000 mg/kg	most Cl remains in the ash: 535 mg/kg

Table 10.7: Comparison of the acid gas concentrations and the daily limits outlined by WID. Data for WID limits: DEFRA (2006a)

Whilst the average SOx concentration determined in these tests was below the WID limit, shown above, the maximum was significantly greater than the daily limit of 50 mg/m^3 and was also larger than the half-hourly maximum value of 76 mg/m^3. This undoubtedly suggests that cleaning to remove this pollutant

would need to be included in the flue gas treatment phase, by utilising FGD techniques, such as sorbent injections or wet or dry scrubbing of the exhaust. Alternatively, SNOx or SNRB could be used to remove both SOx and NOx species. The relatively high proportion of Ca in the SMC casing layer, which was thought to perhaps be beneficial in reducing this pollutant, did not minimise this species to below the policy limits (Altun, *et al.*, 2006). The large proportion of S in the ash, where this element was concentrated, was also not sufficient to remove enough to limit SOx formation. Though both the average and maximum HCl concentrations were low, the highly stringent regulations for this species meant that WID was not always met. The average concentration recorded would satisfy the regulations for the daily mean, although the peak value was much greater. This would however meet the legislation for the half-hourly maximum. As the values were so close to these limits, gas cleaning to ensure lower exhaust gas concentrations would probably be employed. The Cl was found to be concentrated in the ash.

In addition to these, regulations are also defined for a number of other gaseous compounds, such as HF and dioxins, as well as heavy metals, which may be in gaseous form. Unfortunately, the measurement of these was beyond the scope of this project and the facilities available. These could however be monitored during further research into the use of these fuels. As previously suggested, the quite significant sulphur content of the initial fuel may inhibit *de Novo Synthesis* – the mechanism by which dioxins and furans form – thus the concentration of these species is likely to be minimal, even though there is Cl present in the initial fuel (Fielder, 1998). As stated above, the Cl was found to be concentrated in the ash.

Particulate emissions are also regulated by WID, as they can impact human health and the environment. Total emissions need to be within the 10-30 mg/m^3 range on a half-hourly basis, and below 10 mg/m^3 for the daily average (DEFRA, 2006a). Large proportions (~34 %) of the initial material are composed of ash and the amount of flyash collected from the fluidised-bed combustion tests of these fuel pellets was vast. Thus, it is clear that one or more of the particulate removal techniques described in Section 3.4.2.2 will be required to collect the flyash particles from the exhaust gases before they are released to the atmosphere, to comply with this policy. As the particles collected were quite small, highly efficient devices, such as fabric or ceramic filters, would be needed for small and sub-micron particles, perhaps in addition to an initial collection phase, for example using a cyclone, to remove any larger particulates.

10.5 THE ECONOMICS OF USING THESE MATERIALS

The economics of reusing these materials for energy recovery can be broken down into various stages. The main aspects involving expenditure investigated here include: (i) the sourcing and transportation of the raw materials; (ii) the initial processing of the two wastes; (iii) the pelletisation and storage of the materials; and (iv) using the fuel pellets to generate and recover energy, including the costs of flue gas cleaning, ash disposal and other measures required to meet legislation. Many of these were contemplated in Section 5.6. Various aspects of the economic feasibility of this process have been previously considered for these wastes by Ryu, *et al.* (2008).

10.5.1 Sourcing and Transportation Costs

Sourcing the materials would involve the purchase, collection and transportation of the SMC and/or the coal tailings from the mushroom farm/s and one or more collieries to some form of centralised location. Whilst in practice this may either be a specific farm or colliery – one that is central to the collection area as a whole – or a separate facility where these wastes can be processed, for the purpose of this economic analysis, the processing and energy recovery facility will be at the mushroom farm in Whitley. The coal tailings will be sourced and transported here from the lagoons at Maltby Colliery, 25 miles away.

Ryu, *et al.* (2008) estimated the costs of purchasing these waste materials. Whilst the vast majority of these are currently disposed of, which is likely to incur some form of cost to the mushroom farm or colliery, such as landfill tax, such companies may take the opportunity to increase their revenue by charging a small fee for the raw materials. Ryu, *et al.* (2008) suggested this was likely to be £1/t for SMC and £2/t for coal tailings, on an 'as received' basis, which are the values utilised herein. The Whitley mushroom farm produces approximately 150-200 t of spent compost a week; selling this could generate an additional £10,000 each year on top of mushroom sales. The framework conditions outlined by Ryu, *et al.* (2008) were also adopted here. The reference plant for this purpose was assumed to have a production rate of 1.5 t/hr of pellets, resulting in a plant scale of ~12,000 t/a of dried pellets, if plant availability was 90 %. Based on the initial moisture content of the materials and the above purchasing prices of these, the annual cost of sourcing the coal tailings would be £16,800. If the materials are to be processed and used by the mushroom farm, there would be no purchasing costs involved with the SMC.

Ryu, *et al.* (2008) also investigated the transportation costs involved in sourcing SMC and coal tailings; looking specifically at the haulage costs of delivering the SMC to collieries 0-200 miles away. They assumed a cost of £0.074/t per mile, using a tri-axle lorry, which could haul up to 25 t per delivery. As these materials have a high moisture content, the overall transport costs could be dramatically reduced by drying the materials prior to transportation, although this in itself would be costly, as demonstrated below. Increasing the distance travelled increases the transposition costs; Ryu, *et al.* (2008) found that for a 50:50 SMC-coal tailing ratio, 200 miles of haulage would increase overall costs by £14.20 for each tonne of pellets produced. Based on the framework conditions and using the Whitley farm and Maltby Colliery as examples, which are just 25 miles apart, transporting the coal tailings to the mushroom farm would cost £15,540 each year. Increasing the haulage distance to 100 miles would escalate the annual transport costs to more than £60,000 due to the high moisture content of the initial materials. Utilising these wastes at the mushroom farm would eliminate the SMC transportation costs. Also, as the SMC has a higher moisture content and a lower bulk density, it would be cheaper to have the coal tailings delivered.

10.5.2 Initial Processing of the Materials

The initial processing (prior to pelletisation) of the materials once at the facility would primarily involve drying them to an appropriate moisture level. The experimental sections showed that the high initial

moisture was detrimental to both pelletisation and the CV of the subsequent fuel and thus the moisture needs to be reduced from 53 % for the combined materials, to more suitable levels of around 10-15 % prior to pelletisation. On an industrial scale, the waste heat generated from the combustion of these fuels can be used to reduce the moisture content, as considered above in Section 10.3. If this is not practicable, a separate drying system may need to be employed, such as a belt press, although due to economies of scale, this may only be viable in larger plants. The cost of drying fuels, which often constitute a considerable proportion of the overall fuel processing costs (particularly those with high moisture contents, such as these), depends also on the drying system employed. Based on the data from Thek and Obernberger (2004), the drying costs involved for the coal tailings alone would be in the region of £15/t of pellets, where the moisture content would be reduced from an initial ~40 % to around 10 %. For the SMC, where the moisture content is much higher (65-70 % moisture), reducing it to around 20 % would incur costs of over £30/t of pellets (Ryu, *et al.* 2008). These are derived from energy consumption costs for a heat price of approximately £19/MWh (from 2006 figures), where the drying of the materials is not integrated into the energy recovery process. Based on the framework conditions above, the annual drying costs for the initial materials would be £257,985, where the overall moisture content of both materials would be reduced from ~53 % to 15 %, which is more suitable for pelletisation. This could be reduced using waste heat from combustion. An additional drying/curing phase would subsequently be required to ensure a satisfactory fuel quality by further decreasing the moisture content of the pellets; this could be simply achieved by passive drying during storage, which would also be cost-effective.

In addition to the cost of actually drying the materials, the initial investment and maintenance costs of the dryer need to be included. Ryu, *et al.* (2008) estimated that for a tube bundle dryer, depending on the heat demand (1.6-5.3 MWh), the investment would be in the region of £175,000-360,000, comprising the purchasing, servicing and maintenance costs. Based on the moisture contents, the costs of drying and the price of heat (detailed above), it is thought that a heat demand of 2.4 MWh would be required and thus the investment for the dryer would be approximately £240,000.

10.5.3 Manufacturing and Storing the Fuel Pellets

The general expenditure for forming pellets was considered in Section 5.6, which involved the cost of the material (and binder, if used), the pelletiser, the running and maintenance costs and any treatments prior or subsequent to pelletisation, as well as those to any wastes produced. Adding any pre-processing phase, such as drying is not economically favourable, as demonstrated above, although it may be a necessity. The costs associated with pelletisation increase with the complexity of the process; for the purpose herein, a simple ring-die pellet mill will be the technology considered (Ryu, *et al.*, 2008). Based on this pelletiser and the ancillary equipment associated with its use, which would include a cooler, a storage facility and peripheral equipment, it would entail an investment of just over £670,000 (Ryu, *et al.*, 2008). The pelletiser on its own would constitute around £125,000 of this cost. This data was based on the information for the production of wood pellets in Austria and Sweden (Thek and Obernberger, 2004).

Ryu, *et al.* (2008) estimated the annual pellet production costs to be in the region of £165,000 for the production of 24,000 t of pellets; it is thus thought that producing half this quantity would result in a cost of around £80,000 for this operation. Derived from the data in Ryu, *et al.* (2008), the annual storage costs are thought to be in the order of £15,000; an annual operating cost of around £170,000 was also calculated therein, for the provision of personnel, which would cover administration, marketing, insurance and taxes. It was determined that on a commercial scale, the cost of 50:50 wt% ratio SMC:coal tailing pellet production (based on capital, consumption and operating – including the dryer and pelletisation stages – and maintenance costs) is thought to be about £44/t of pellets excluding transportation costs, increasing to £58/t of pellets with transporting the SMC 200 miles (Ryu, *et al.*, 2008). The consumption and operating costs calculated herein for the production of 50:50 wt% ratio SMC:coal tailing pellets was £29.58/t, increasing to £32.41/t with purchasing and transport costs.

The energy consumption during pelletisation can range widely, but is not usually very high, although this does depend on the pressure and complexity of the operation, as well as on plant capacity. What is often the primary factor affecting the overall energy consumption is the degree of drying. Specific heat consumption can be in excess of 1000 kWh/t of pellets, predominantly used for drying (Thek and Obernberger, 2002).

Although a simple pelletisation operation – for example with no pre-processing, binders or elevated temperatures – is cheap, the best quality pellets are not necessarily formed, as seen herein (Moore, 1965). The starch binder is thought to be cost-effective, in that it is cheap to procure and is easy to apply (can be simply combined with the two materials during the mixing phase) whilst improving pellet qualities, such as tensile strength. Whilst drying and pelletisation seems to already be a costly operation, as the moisture contents for SMC and coal tailings are quite high (65-70 % and ~40 % respectively), the use of elevated temperatures or steam to enhance pellet properties in addition to this would considerably increase overall production costs, through greater process complexity resulting in higher capital and operating costs. Excess heat or steam from the energy recovery process could be utilised to minimise costs. The extra expenditure used for generating such temperatures could however be recovered by utilising lower pressures. The use of either elevated temperatures or a binder at the pelletisation stage is strongly dependent on the comparative costs of these options and the degree of improvement required in product quality; no additional means of quality improvement were assumed here.

10.5.4 Using the Fuel Pellets and Flue Gas Cleaning to Meet Legislation

Once the pellets have been formed, energy needs to be recovered from them, via combustion. Thus an incinerator with heat recovery systems and energy generators would have to be purchased and maintained. Additional equipment, such as fuel feeders would need to be integrated within this system. Although procuring such a reactor would result in significant expenditure, the energy and heat generated could be used to meet the requirements for a mushroom facility, which involves highly controlled

conditions for mushroom development and growth. The generation of on-site heat and power in an EfW facility would not only negate the costs usually incurred for purchasing power from the national grid, but would also offset, at least in part, the initial and maintenance costs of the facility. McCahey, *et al.* (2003) considered that the combustion of SMC in a fluidised-bed would cost £6.80/t. As seen above in Section 10.4, a certain degree of flue gas cleaning would be required, specifically to remove particulate matter from the exhaust to minimise its impacts on the environment and also on human health. As demonstrated previously, much ash is generated from the combustion of these fuels, thus efficient collection systems would be essential, yet costly, to comply with WID. The removal of acid gas species, although minimal, is also likely to be required. This would obviously incur a certain amount of extra costs. SCR, for example, although highly efficient, it is also extremely expensive – £600/t of NOx removed (Coal R&D, 1997). Whilst NOx removal might not be a necessity, treating the flue gases for SOx and HCl does appear to be a requirement.

10.5.5 Overall Cost of Using These Materials

The above outlined the breakdown of the various costs of sourcing the materials and transforming them into a usable fuel. The initial investment involved with the purchase of the dryer, pelletiser and ancillary equipment would incur a total cost of just over £900,000, as shown in Table 10.8. This does however include any service and maintenance required to the machinery, which are thought to remain serviceable for 10-15 years. The annual expenditure on materials, transportation and the use of the equipment would require another £400,000 of capital. Based on transporting the coal tailings from Maltby Colliery to the mushroom farm in Whitley, for processing to form 50:50 wt% SMC-coal tailing pellets, is thought to cost £30-35/t of pellets manufactured. Further capital would be needed to design, manufacture and utilise a suitable combustor for this fuel, as considered above.

COST INCURRED	EXPENDITURE		
	Initial	Annual	Tonne of Pellets
Purchasing Coal Tailings	-	£16,800	£1.47
Transporting 25 miles	-	£15,500	£1.36
Purchase of Dryer	£240,000	-	-
Initial Processing – Drying	-	£258,000	£22.50
Purchase of Pelletiser	£125,000	-	-
Purchase of Ancillary Equipment	£546,600	-	-
Pelletisation	-	£81,000	£7.08
Storage	-	£16,600	£1.45
TOTAL COST	**£911,622.00**	**£388,021.50**	**£33.86**

Table 10.8: A summary of the initial, annual and per tonne of pellet costs for producing these fuel pellets.

10.6 DISCUSSION

The results herein show that the experimental data can be replicated with a good deal of accuracy within the FLUENT model for most of the parameters considered, providing appropriate inputs are used. By executing a range of model scenarios, the most suitable conditions found were based on the closest

matches to the experimental gas and temperature data. It was found that a good degree of accuracy could be achieved for thermocouples T3, T4, T7 and T8, which had minimal percentage errors for the most precise model cases (~0.98 %). The oxygen and CO_2 gas concentrations in the exhaust were also simulated quite well. Due to the simplistic nature of the computational model, however, it predicted that no CO would be present in the exhaust gas stream, as there was still oxygen left in the system. The combustion efficiency would thus be very high. It suggests that all combustion reactions would go to completion and all CO and other combustible species would be fully oxidised, due to sufficiently turbulent mixing. The experimental results from the laboratory-scale fluidised-bed contradict this, although by scaling up the reactor and including secondary air jets, the combustion efficiency could be improved and CO markedly minimised. The modelling of the elutriation and entrainment of particles from the sand bed showed that a sufficient freeboard was provided, to minimise bed particles escaping with the fast-flowing primary air and flue gases. This was corroborated by the experimental data, as no sand particles were found in the cyclone. The less dense flyash particles, however, were shown to reach the freeboard and leave the system at the exit duct; flyash was indeed collected in the cyclone during such experiments, in copious amounts. There are limitations associated with all models, as briefly suggested above, and FLUENT and its applications are no exception. For the purpose of this model, the fuel was imitated as propane, rather than SMC-coal tailing pellets, as the model is only able to look at the gas phase, thus the fuel had to be represented as a gas. Whilst the experimental results suggest partial combustion was taking place to some degree, due to the presence of CO in the gas analysis and unburned particles in the flyash, the model assumed all combustible materials were completely oxidised. There was not sufficient mixing within the reactor to complete all combustion reactions, whereas in the model the fuel gases and oxygen were adequately mixed to complete fuel burnout.

The heat and mass balance equations utilised showed that the addition of the higher CV coal tailings to the SMC was vital for the generation of sufficient heat and power, for the furnace set-up considered. Significantly more energy could be generated from the combination of these materials in pelletised form. It was demonstrated that a single mushroom farm, such as Monaghan Mushrooms in Whitley, could combine its waste with a similar amount of coal tailings from a nearby colliery, such as Maltby, to generate 0.5 MWe, which would go towards covering their outgoings concerning the heat and power required for the careful control over the growing conditions.

The legislation concerning harmful gases, such as NOx, SOx and HCl are regulated by WID, thus their release to the environment from an EfW facility combusting SMC-coal tailing pellets needs to be controlled. The comparison herein demonstrated that whilst the production of such gases from this source was minimal compared to those of other fuels, gas cleaning would be required to meet these regulations – specifically for SOx and HCl. In addition to these flue gas cleaning mechanisms, the minimisation of other harmful releases, such as CO and fine particulate matter would be a necessity, by integrating additional technology into the system. The extra equipment required to comply with such policies mean

further costs are added to the overall process, which as the economics have previously shown, are already quite high. The calculations concerning the process economics revealed that whilst the initial investment was vast, it was the drying of the materials that would incur the largest annual cost; of the £400,000 that would be required each year to manufacture 12,000 t of pellets, over half would be used on drying alone. As this makes up such a significant proportion of the total manufacturing costs, it is likely that this will be the critical factor which determines whether this process is viable or not. It therefore appears necessary to employ a less energy intensive drying process to minimise overall production costs. The transportation costs were fairly minimal by comparison, but on a larger scale of operation, the haulage distances would undoubtedly be much greater and would thus further increase the cost of pelletisation from £30-35/t. A more economical drying process would alleviate this somewhat. Bearing in mind this fuel price, it means that the direct cost of electricity production would be approximately 3.5 p/kWh, though this does not take the capital and operating costs into consideration; thus this could be competitive since current prices are in the region of 18 p/kWh.

10.7 CONCLUSIONS

The industrial implications of using these wastes as fuels were investigated in numerous ways. Initially, FLUENT modelling was used to replicate the experimental pellet combustion data. By manipulating the input conditions, the experimental results were well replicated by the model; as there was excess oxygen provided, the model assumed that no incomplete combustion took place, which was not the case for the experimentation, as both CO and unburned particles were present. The oxygen and CO_2 concentrations however were comparable. Furthermore, the temperatures, particularly those modelled near the bed of the combustor had a good degree of accuracy with minimal percentage errors of ~3 % for the most precise model cases. The simulations of particle elutriation and entrainment showed a sufficient freeboard height was provided to prevent bed particles escaping with the flue gases. The smaller, lighter flyash particles however were modelled leaving the combustor, as with the experimental results. Secondly, heat and power generation was computed using mass and energy balances for a theoretical furnace, boiler and turbine set-up, which included a drying phase for the materials using excess process heat. 5 MWe could be generated using an SMC-coal tailing pellet feedrate of 200,000 t/a.

The process economics were calculated for the annual production of 12,000 t of fuel pellets – comprising of sourcing, transporting, drying and processing these wastes. The initial cost of purchasing the equipment was vast, around £900,000. An additional annual expenditure of £400,000 would also be required for buying, transporting, drying and pelletising the materials, as well as for the service, maintenance and operation of the machinery. This means that the pellets would cost £30-35/t to produce – £22.50 of which would be used simply for the drying. The subsequent combustion and clean-up of residues would incur further costs. Flyash removal would be necessary, in addition to the elimination of certain acid gases species, as the comparison of the experimental data concerning NOx, SOx and HCl to WID limits revealed that some form of gas cleaning would indeed be needed.

11

DISCUSSION

11.1 INTRODUCTION

This chapter firstly contains an in-depth overall discussion of both the experimental programme and the complimentary modelling work, initially in relation to the project aims. The results obtained from the experiments performed have been reported and analysed in the previous chapters; herein, these results and a number of implications, which require addressing concerning these, are discussed. This will again be categorised according to the three experimental stages. The modelling simulations conducted in FLUENT and the theoretical work concerning heat and power generation and the economics of producing these fuel pellets are also considered. Secondly, the industrial applications of this work are considered; the use of SMC-coal tailing pellets as a source of energy will have technological implications, as well as impacts on the environment. The implications of the cost of producing and using these pellets also require examination, as does the perception of the public and its possible acceptance as an energy source.

Lastly, an evaluation of the research is presented. The main sources of error within the experimental and theoretical results are considered and the limitations are outlined, upon which future work can focus. Areas for improvements are also identified.

11.2 OVERALL DISCUSSION OF EXPERIMENTAL RESULTS

In this section, an overall discussion of the main experimental stages is presented: (i) material characterisation; (ii) various aspects of pelletisation; (iii) in-depth investigation into fluidised-bed combustion of the SMC-coal tailing pellets; and (iv) the other thermal treatments performed on the materials. These are first considered in relation to the aims set out for this research.

11.2.1 Discussion of Project Aims

The aims and objectives of the research were presented in Section 1.5. This identified the four primary aims and outlined the main objectives for each. The first was to complete a broad literature search regarding biomass and its related legislation, then focus on the two waste materials. Biomass and bioenergy in general were investigated in detail, including many wastes that are used for energy recovery. Furthermore, the relevant legislative policies relating to bioenergy generation and the use and disposal of materials, such as those utilised here were then examined. The emissions limits outlined in the Waste Incineration Directive were subsequently employed to compare the pollutant concentrations from the thermal treatment of these wastes. The formation, properties and potential uses of SMC and coal tailings were also examined; the material characteristics that were ascertained from various sources in this section were also subsequently used as comparisons for the experimentally-determined composition of these wastes herein. From this, the gap in current knowledge was identified and a clear area warranting further research was defined. This review of pertinent literature leading to the identification of a valuable, yet under-researched field fulfilled the first project aim.

The second aim was to thoroughly investigate relevant theoretical topics, including thermal treatments for energy production and their associated clean-up systems, fluidisation and fluidised-bed combustion and pelletisation. Each was considered in great depth and formed a vital background upon which the subsequent experimental sections were based. Combustion, gasification and pyrolysis mechanisms were identified and were consequently performed on the materials at hand. Typical pollutant species were also identified, both in the literature and in the experiments carried out later. The fluidisation chapter allowed various fundamental theoretical equations to be discovered, which were then utilised during the fluidised-bed combustion studies of the materials. The pelletisation chapter identified key pelletisation parameters, which are known to control product quality. Methods of quality assessment were also noted, although standard methods have not been established for all criteria. Optimum pelletisation conditions could then be determined for the SMC, coal tailings and the mixture, based on these experimental methods. This extensive study of such topics accomplished the requirements set out by the second aim.

Thirdly, a wide range of experimental methodologies were executed, based on the literature and theoretical topics reviewed. The material characteristics were analysed using standard methods, and were compared to the data obtained in the literature review accordingly. The pelletisation and thermal treatment of the wastes were also based on the theoretical review of these topics, where an extensive series of variables were tested and optimised for each. Based on this experimental work, and also to compliment it, the industrial applications and implications of using these fuels were examined. This included theoretical and mathematical modelling (FLUENT and heat and mass balances), a consideration of whether the pollutants produced would meet the legislation outlined in the literature review, namely WID, and estimating the cost of processing and using these fuels. These comprehensive experimental and theoretical investigations accomplished the needs of the last two aims.

11.2.2 Material Characterisation

The first phase of the experimental investigation was concerned with characterising the two materials. This involved performing a number of standard tests on the coal tailings and the SMC; as the SMC had two distinctly different components (casing layer and substrate), these were analysed separately.

The compositions of the materials were determined using ultimate, proximate and elemental analyses; results for several of these had also been reported in the literature, which provided an archetypal basis for comparison. Despite the obvious differences in appearance between the SMC layers, their compositions were surprisingly similar, in terms of the ultimate and proximate analyses. The coal tailings were distinctly different, where the fixed carbon present was higher and volatiles significantly lower than that of the SMC. The coal tailings had a CV comparable to sub-bituminous coal, as well as to other coal tailing samples identified in the literature. The CVs of the two SMC layers were similar to each other and the biomasses discussed previously; they were also analogous to those of Williams, *et al.* (2001a). These were, however, significantly lower than the coal tailings and thus additions of SMC to the fuel pellets decreased their overall energy content. This did have benefits, in that it increased pellet strength due to the variation in particle size and type, and enhanced the carbon-neutrality of the fuel, which is highly advantageous when this decreased the CV. The moisture content of all samples were extremely high, thus drying was an essential process to form suitable fuel pellets from these materials, as poor quality ensued if this was not reduced to more appropriate levels. This would also be the case for commercial production. Inferior combustion due to lower CVs would also result. Additionally, the ash contents were high, which affected combustion in a detrimental way, as there was less combustible material available; furthermore, this produced significant amounts of particulate matter during combustion. A potential application of this ash was considered in the literature review, concerning its use as an activator for PFA.

Whilst the S content was quite high for both SMC layers and was also present in the coal tailings, SOx were not thought to be a significant problem during combustion, for two key reasons: firstly, the S was primarily found as inorganic forms – sulphates, such as gypsum, which does not decompose until high temperatures are reached (in excess of 1450 °C); and secondly, the very high proportions of Ca, particularly in the casing layer of the SMC, determined in the elemental analysis, may be beneficial as it can effectively capture S or reduce any SOx compounds that are produced, replicating the function of sorbent injections and scrubbers during flue gas cleaning technologies, though P may interfere with this (Williams, *et al.*, 2001a; Elled, *et al.*, 2006; Altun, *et al.*, 2006). The SOx concentrations monitored during the combustion tests were minimal (~12 ppm). This S present could also be beneficial in inhibiting *de Novo Synthesis*, preventing the formation of dioxins and furans, as Cl was present in both SMC layers. The elemental analyses allowed a more in-depth comparison of the materials, identifying elements not found in the ultimate analysis, particularly those that may cause problems during combustion; this also highlighted the differences between the two SMC layers. Alkali metals, specifically K and Na were prominent, the oxides of which cause problems of slagging and fouling; the Alkali Index

computed using the concentration of these metals in the flyash samples from the combustion tests showed that their concentration was sufficient to probably cause such issues. Fe, Si, P and Al were found in significant quantities, and if in oxide form, these too can contribute to slagging, fouling and ash agglomeration. Furthermore, Cl, which was also present in the initial materials, generally remained in the ash; whilst this would prevent harmful species, such as dioxins, furans and HCl forming, the latter of which was experimentally confirmed, it may also increase the tendency of the ash to agglomerate.

From the particle size analysis, it is thought that when the materials are pelletised together, the additions of the long SMC substrate fibres to the powdery substances of the coal tailings and casing layer, which had similar particle size distributions, could enhance the strength and integrity of the pellets due to interweaving. On later testing of such pellets, this was found to be the case. Often large agglomerates of the coal tailings and SMC casing layer could be found within the samples, and this too may have also aided particle binding within the pellets and enhanced their strength.

11.2.3 Pelletisation Case Studies

Compression was used to form the pellets in the manual pelletiser, according to the stages outlined in the compacting sequence in the review of pelletisation theory. This section also identified key pelletisation parameters and many of these were tested for SMC, coal tailings or mixtures of the two. Moisture content, pressure, holding time and pellet composition were outlined as the key test variables and the optimum conditions for pelletisation were determined. The effect of changing these was assessed by determining the tensile strength, density and durability of the pellets; these assessment criteria were chosen as they were used in a wide range of literature considered. Pellet pile heights were also estimated.

It was found that as pellet density increased, tensile strength generally improved, affected by many variables; this did not however necessarily equate to increases in mechanical durability (Lehtikangas, 2001; Obernberger and Thek, 2004; Rhén, *et al.*, 2005). As the moisture was found to be one of the most influential variables in determining pellet strength, the ideal moisture content was found to be 10-11 % for coal tailings and slightly higher (15 %) for SMC, as it varies between materials. This concurs with the work of Sastry (1993) and Li and Liu (2000), who suggested that the optimum moisture range is quite narrow. It is vital that this is controlled to ensure optimal particle plasticity is achieved and the particles are an ideal distance apart. High or low moisture contents were found to be detrimental to pellet quality, because the void space between particles was too large or plasticity was reduced. After pellet formation, air-drying to 2-3 % moisture was also necessary to further enhance their qualities and harden them. This is a common post-pelletisation treatment, especially for fuels, as it enhances their CV; it can however be costly, as demonstrated by the economic analysis of the production of pellets from these materials. The importance of drying coal tailing briquettes was emphasized by Radloff, *et al.* (2004). Thus drying is obviously necessary, in terms of pellet properties (tensile strength and CV) and will be required for the commercial use of these fuels, whatever the economic implications.

Pressure was another highly important parameter; as the compression force increased, the particles started to deform and as a result, the densities and tensile strengths were greater. There did become a point, however, when large increases in pressure led to fairly minimal improvements in these properties. This was primarily due to the initial compression rearranging particles when void spaces were large, whereas the later compression could not fill any more interstices, as they were very small – usually smaller than the particle sizes, and particle deformation and breakdown would occur only at extreme pressures (Jones, 1969). For these materials, the point where the graph started to level off was 6000 psi (41.4 MPa), classified as low pressure pelletisation (Rieschel, 1963). The influence of particle size and particle size distribution was therefore also apparent. As a result, the pelletisation pressure chosen to be employed should be a balance of ideal product properties and the energy costs of the pelletisation; increasing the compaction pressure beyond its useful level, in terms of enhancing pellet density and strength, is not advisable. Concurring with the above discussion of pellet moisture, tensile strength was greater for dried pellets formed at all pressures. Holding time is thought to be more significant at lower pressures, such as those used for the pelletisation of these substances. Pellet density herein did increase slightly as holding time lengthened, although the effect on tensile strength was less apparent; similar results were found by Li and Liu (2000) in the literature review during their investigation of other biomasses.

When the SMC was pelletised on its own, pellet tensile strength was quite low; this however was significantly improved by removing the casing layer, although this also increased the variability in the results. This may suggest that it is advantageous to only use the substrate in the fuel pellets, as this enhances pellet strength and also their CV, as the casing had a lower energy content. This, however, is not always practical, as it would be difficult to separate the layers without contamination and also raises the question of what to do with the remaining SMC. Something that was found for the SMC pellets but not for the coal tailing pellets was that swelling was considerable and dependent on the moisture content; coal tailing pellets remained constant in size, with swelling or shrinking generally less than 1 %, whereas SMC pellets expanded by up to 30 %, particularly those with high moisture (≥20 %). This, as well as pellet drying, considerably lowered pellet density. Additionally, cracks appeared almost immediately after pelletisation, as well as during drying. Despite this, the tensile strength and durability of these pellets were quite high, perhaps because the fibrous nature of the substance was able to better distribute the forces encountered during these tests. SMC pellets tended to deform, yet remained intact, whereas coal tailing pellets simply broke when the forces became too great.

Due to the varying elemental compositions and the differences in properties, it was necessary to establish the optimum SMC:coal tailing ratio. Varying proportions were tested for tensile strength and density and a 50:50 wt% ratio was found to produce the best results, when the initial moisture was adjusted (~15 %). Sufficient mixing was required to ensure they were homogeneous. This fraction of the materials allowed the best qualities of both to be combined into a single pellet and aided their strength and integrity; these were the strength of the coal tailing pellets with the flexibility of the SMC fibres. This meant that

breakages were less likely and deformation occurred instead, where the pellets were still intact and coherent. Pellets made at high pressures and then air-dried were the most durable.

The properties of these optimum pellets, in terms of their tensile strength and durability, meant they should be able to endure handling and transportation reasonably well. It was found however that handling them still produced vast amounts of dust. Ways in which to reduce this friability and improve pellet quality were investigated. A simple, cheap and effective way of doing this was to add a binder. Organic and inorganic binding agents were considered; both starch and caustic soda were found to be cost-effective, where 1 wt% of starch improved overall pellet quality more significantly. This was also found to have less of an impact on pellet combustion, as the Na in the caustic soda increased the Alkali Index and reduced the ash fusion temperatures. The use of steam conditioning and elevated temperatures were also found to be beneficial in improving the overall quality of the fuel; these were however deemed to be much more expensive options. Seeing that the economic analysis determined that pellet formation would already incur considerable expenditure, the addition of further costly processing would most likely make the use of these unviable, unless the heat or steam came from the energy recovery process. If it was felt necessary that pellet quality needed to be enhanced beyond the level that could be provided by simply manipulating the pelletisation variables, then the use of starch seems the most practicable option.

11.2.4 Fluidised-Bed Combustion of the Fuel Pellets

Based on the initial investigation into the thermal treatment of these fuels, considered subsequently, it was found that combustion in a fluidised-bed was more efficient than that in a packed-/fixed-bed reactor. Furthermore, this type of combustor is better suited for fuels with high ash contents, determined for these fuels from the proximate analysis. Pellet combustion was also deemed more viable in both reaction vessels than that of the unpelletised, raw SMC on its own, as the addition of the higher energy content coal tailings was vital. Pellet combustion took longer for an equivalent amount of SMC fuel, due to their enhanced energy density and CV properties. This confirmed the results of Wereko-Brobby and Hagen (1996), McKendry (2002b) and Bridgewater, *et al.* (2002), who stated that combusting raw fuel without pre-processing leads to lower efficiencies, whereas co-combustion is advantageous for achieving high conversion efficiencies.

The combustion of SMC-coal tailing pellets in a laboratory-scale fluidised-bed thus required further examination. Through identifying key combustion variables – the pellet feedrate, the air flowrate and the sand bed depth – a series of tests were devised to determine the optimum conditions for this reactor. Eleven cases were designed to investigate the air ratio, which was dependent on both the pellet feedrate and air flowrate. It was found that the reactor was quite inefficient, as high air ratios, much larger than those used in commercial combustors, were needed to gain sufficient fuel burnout and good combustion efficiencies. Whilst high efficiencies were achieved, up to 98 % using an air ratio of 3.76, high levels of CO (2.5 %) and thus low efficiencies (~87 %) were found for smaller proportions of excess air (air ratio

of 1.61). Using an optimised industrial-scale combustor, which would include turbulent secondary air jets to redistribute this excess oxygen, could significantly improve such results. The cases to evaluate the sand bed depth found that the deeper bed of 0.27 m was less efficient (η_{CE} = 91 % compared to 95 % for a bed depth of 0.22 m) and also produced, on average, notably more pollutants. The deeper bed for the initial tests was 0.30 m and achieving adequate fluidisation at this depth was notoriously difficult. The bed-depth-to-diameter ratio was thus crucial. This would mean that for a larger reactor, the bed could be much deeper to improve the efficiency, whilst maintaining a bed-depth-to-diameter ratio closer to 1.

The temperatures generated during combustion were conspicuously greater in the bed than the freeboard, as the densified fuel pellets overcame the upward flow of primary air to burn in the bed and the high volatile content of the SMC fraction would combust rapidly here. Char burnout would take much longer, as discussed in the review of combustion theory, to maintain such bed temperatures if there were pauses in fuel feeding. It was thought however, that small unburned char particles were often elutriated from the bed, which would account for the high concentration of combustible material in the flyash, compared to the high efficiencies calculated based on the flue gas concentrations. This pattern of temperatures was also noted for the FLUENT simulations. Much of the literature also confirmed such findings, although certain examples were discussed where freeboard temperatures were significantly greater.

Acid gas species – NOx, SOx and HCl – were monitored for these tests. For the commercial use of these fuels, the emissions from combustion must comply with WID, as outlined in the legislation section. Though the concentrations were not very high, for the reasons explored above, it was found that for SOx and HCl in particular, gas cleaning would be a necessity to comply with this directive. The average values for both these were low, 12 ppm for SOx and 5.3 ppm for HCl, yet the stringent legislation meant that the maximum values occasionally produced were beyond the limits specified. Gas cleaning would thus be necessary, regardless of cost. Despite the Ca content of the initial material, which was thought to further reduce SOx emissions, this appeared to not be able to minimise SOx concentrations below the required threshold. This may be due to interference from the P present or because the form of S was not able to react with the Ca to initiate its capture. NOx removal would not be mandatory, since the maximum levels generated from these wastes (91 mg/m^3) were considerably below the limits set out in WID (200-400 mg/m^3); it may be included however to further minimise any negative environmental impacts. Whilst the S and Cl were found to be concentrated in the flyash, N could not be accounted for in this manner. It was therefore assumed that N_2O would have formed, as this could not be monitored; as considered previously, fluidised-bed combustors are particularly prone to this and therefore this would be a reasonable assumption. Its elimination from the gases would be beneficial as this is a greenhouse gas.

Flyash samples were also analysed for these tests. Vast amounts of ash were collected in the cyclone; as predicted from the material characterisation, there were considerable amounts already present in both the SMC and the coal tailings, around 34 % for the fuel pellets. Particulate collection will thus be a much needed gas treatment, as these must be removed from the flue before release to the atmosphere.

Cyclones, as considered in the review of flue gas cleaning, generally have lower efficiencies, and consequently an alternative method to that used here will need to be employed to ensure unwanted release to the environment. Ash analyses identified elements that were likely to cause issues in the combustor, such as slagging, fouling and agglomeration. These included K, Na, Al, Si, Fe, P, S and Cl, which were concentrated here from the initial materials; such problems were predicted, considered above, due to the composition of the fuels. The Alkali Index was computed and established that the presence of K and Na in the SMC and coal tailings was sufficient to induce the likely slagging and fouling of the system. The addition of supplementary Na through the inclusion of a caustic soda binder increased the AI of the fuel, although not to such an extent that certain fouling would occur. The high proportions of Fe and Al, and to a lesser extent, Si, would also increase the likelihood of these detrimental deposits occurring in the combustor if in oxide form. Many elements listed above would also promote ash agglomeration.

The impacts of the caustic soda and starch on pelletisation were apparent, where starch performed consistently better as a binder. Whilst just 1 wt% of both negatively impacted combustion, in that the efficiency was reduced (from 95.0 % to 88.7 %), NaOH also had a detrimental influence on the ash properties. In addition to increasing the AI, the added Na also lowered the ash fusion temperature, making agglomeration more probable. Starch was thus better able to improve pellet quality, as well as having fewer impacts on combustion; if a binder is required, starch would be cost-effective.

11.2.5 Other Thermal Treatment Technologies

Four combustion cases were initially performed in the fluidised- and packed-beds. The fluidised-bed tests were successful in that both the pellets and the raw SMC were easily combusted; the results showed that the initial temperatures in the bed and freeboard could be maintained, providing appropriate air flowrates and fuel feedrates were employed. Both fuels underwent mainly complete combustion, as excess oxygen was present and minimal CO was monitored in the exhaust. Of these two tests, the combustion of the pellets was superior. The combustion of these materials in the packed-bed was also successful. As suggested by McKendry (2002b), hot gases at 800-1000+ °C were produced in all cases, which is sufficient for the generation of heat and power. The four key constituents of these fuels (moisture, volatiles, fixed carbon and ash) were discovered on a percentage basis in the material characterisation phase and the stages of reactions that these underwent during combustion were clear, reflecting those outlined by Shin and Choi (2000) in Figure 3.2. The materials were dried prior to their combustion, thus the removal of the inert moisture and devolatisation were the first processes to occur by the additions of heat from the burner. The burning of the volatiles in the freeboard was seen in the temperature increase in this area. During this stage and the carbonaceous char combustion, the CO_2 concentration was high, indicating the complete combustion of these components, as summarised in Equations 3.1 and 3.2. After this was complete, the ash remained on the grate. As with the comparison of these materials in the fluidised-bed, pellet combustion was also superior in the packed-bed, as the air flowrates had to be adjusted several times during SMC combustion to ensure the flame was not extinguished.

SMC gasification and pyrolysis enabled a comparison between various thermal technologies. The processes outlined in the theoretical background for these treatments could be clearly identified. SMC gasification involved its partial oxidation, which, as described in Chapter 3 involved the process whereby a solid, fairly homogeneous combustible material (fuel) was subjected to high temperatures to form a combustible, gaseous fuel. Of the three modes of gasification, air was used so that the temperatures required to initiate gasification reactions were low. Due to this, however, the CV of the fuel gases were also likely to be low, as much atmospheric nitrogen was present in the gas. The key constituents of gasified biomass were outlined in the theoretical background; Ramage and Scurlock (1996) state these are H_2, CO, CO_2, CH_4 and other hydrocarbons, as well as nitrogen, if air is used. The nitrogen dilution due to the use of air was clearly seen for this system, where the fuel gases, such as CO, H_2 and CH_4 only made up a maximum of 50 % of the total gases leaving the system at any one time. In addition to CO production, significant amounts of CO_2 were also formed, due to the complete oxidation of C, expressed in Equation 3.6. As some H_2 and CH_4 were formed, the water-gas shift reaction, hydrogenation and methanation were also occurring, as outlined in Equations 3.6-3.8, although only in the latter stages.

Pyrolysis – thermal degradation in the absence of air – was performed on the dry SMC. The significant yields of char (43.33 %), pyrolytic oils/liquid (34.71 %) and syngas (21.96 %), coupled with the low maximum temperature (< 600 °C) and the moderate heating rates (10 °C/min) show that conventional pyrolysis was used. This type of pyrolysis produced volatile matter that formed the syngas and char with a high energy density (~8 MJ/kg). These products, particularly the char and the CO and H_2 components of the syngas were formed by exothermic carbonisation and a water-gas reaction (Equations 3.3 and 3.4). The liquid phase had a low energy content of 2.98 MJ/kg.

11.2.6 FLUENT Modelling of Combustion

The FLUENT modelling took place in two main phases: firstly, the simulation of the experimental conditions for comparison and secondly, the assessment of the TDH. Many model conditions were manipulated to ensure an accurate prediction of the experimental results. Based on the experimental data for temperatures and fuel characteristics, several cases were modelled, where the best results were gained for a wall temperature of 448 K and when gravity and inlet diffusion were on. This case gave an accurate picture of the temperatures, where the error was 3 % between the experimental and modelled data. The errors were larger for the gas concentrations, as the model assumed all combustion reactions would be complete, due to the excess oxygen present. As such, there was no CO in the model predictions. The oxygen concentration was lower than those determined experimentally, out by 0.2 % (an error of 5 %), and thus the CO_2 concentration was greater, out by 2 % (an error of 13.7 %). By using appropriate input conditions for the model simulations, the errors could be significantly reduced. This was most apparent for temperature, where a high degree of accuracy could be achieved with apposite conditions – the 3 % error, noted above – compared to an error of around 15 % for cases where the inputs were less suitable. This showed that the experimental results could be successfully simulated using such a model.

Using this as a basis, the TDH of particles was estimated. The sand particles that elutriated from the bed returned before they were able to reach a significant height (up to 0.22 m for the fastest inlet velocity) and were thus not removed from the system. This corroborated the empirical data, as there was not any sand bed particles collected in the cyclone, and thus an adequate TDH was provided. Flyash particles, which were significantly smaller and lighter than the sand, elutriated and were carried out with the exhaust gases; such particles exhibited a swirling and re-circulatory motion at the combustor exit, due to their tangential momentum in this region of the reactor.

11.2.7 Heat and Power Generation and Economic Analysis

Heat and power generation was calculated based on mass and energy balances for a range of scenarios, where the fuel throughput was varied; small- to large-scale operations were compared. As found with the experiments concerning the use of SMC alone, the results here were also inferior, where power generation was low; only 0.09 MWe could be generated with an annual SMC feedrate of 10,000 t. With the addition of 10,000 t/a of coal tailings in pelletised form, however, energy recovery could be increased to 0.5 MWe, again demonstrating the need for the inclusion of the higher CV material in this fuel. Larger scales were also considered. As stated previously, there is approximately 200,000 t/a of SMC available in the UK; assuming all this could be combined with an equivalent amount of coal tailings at a centralised facility, electricity generation would be in the region of 10.5 MWe. The transportation costs of such a concept would be huge, as the locations of UK mushroom farms are widespread (Figure 2.18). This would be likely to make the overall cost of the processing so high that it would be economically unviable.

The economic analysis revealed that whilst the purchasing and transportation costs of sourcing these materials could be high, depending on the haulage distance, they were minimal compared to the amount that would be spent on drying. Reducing the moisture content of the coal tailings from 40% and the SMC from around 68 % to 10-15 % would be expensive – accounting for ⅔ of the overall annual expenditure on pellet manufacture, thus a less energy intensive drying method would be beneficial. This initial drying would cost in the region of £20-25/t of pellets produced. This increases the estimated production costs from £11.36/t of pellets to £30-35/t. This was based on a facility producing ~12,000 t/a of pellets, which could be generated from the waste compost from the Monaghan Mushroom farm at Whitley and an equal amount of coal tailings sourced from nearby Maltby Colliery. Based on the heat and power calculations for this amount of fuel, electricity production would be in the region of 0.26 MWe.

11.2.8 Overall Discussion of the Research Findings

Though this research has been separated into various experimental and modelling sections, linkages between these can be made, to demonstrate the comprehensiveness of the research programme. As illustrated, the combination of SMC and coal tailings in pelletised form has obvious benefits; the CV and bulk density are increased, the SMC is CO_2-neutral by nature and the moisture content and other properties can be controlled for both substances. Whilst this has been demonstrated to be feasible in a

practical sense, it may not necessarily be economically-viable due to the high moisture contents of both fuels. An alternate, less energy intensive drying system would greatly aid this process and make it more possible; the economics may be further enhanced however with increasing amounts of landfill tax on materials, such as SMC. Sourcing, processing and utilising the materials locally in small-scale energy recovery facilities appears a more practicable option to avoid the high transportation costs of hauling low density materials long distances. This would make sense for specific farms, which could use the waste produced on-site to generate energy for their own needs. As it is vital to find a sound waste management solution to secure the future of the industry, using these wastes would minimise the expenditure of buying energy from the grid and mean that the industry could be expanded to meet growing demand.

These fuel pellets can then be used in a fluidised-bed to generate heat and power, without the need for supplementary fuels, thus the energy recovery facilities would only need to purchase coal tailings to generate a satisfactory amount of energy for their own use. By utilising appropriate combustion conditions and optimising the process with secondary air jets, very high combustion efficiencies can be achieved for effective energy recovery. Gas cleaning to comply with WID should not be problematic as the acid gas emissions generated were not greatly above the limits outlined; particulate removal would be needed and there are several highly efficient systems available for such purposes, as reviewed earlier.

11.3 INDUSTRIAL APPLICATIONS: IMPLICATIONS OF THE FINDINGS

11.3.1 Technological Implications

The experimental results have significant applications for industry, in a variety of areas. The technological implications start at the beginning of the process, with the formation of the pellets. Drying, as previously considered, is essential as the moisture content is significant; this will most likely require active drying, using heaters, belt presses or another form of technology. Whilst this has been demonstrated to be expensive, the materials cannot be pelletised or used as fuel without it. The pelletisation technologies have also been described in preceding chapters, both in terms of those widely available and those used herein; compression is suitable for pelletising these materials, using a continuous process to be more cost-effective. The pellets can be stored safely in piles for 1-2 months whilst they dry further and await combustion, although longer storage periods should be investigated to ensure microbial growth does not degrade pellet quality.

Although the thermal technologies utilised were trial runs and thus only for demonstration purposes, they have proven that these materials can be successfully employed as energy sources, particularly in pelletised form. The reactions taking place during combustion were self-sustaining and occurred at considerable temperatures, high enough for the production of useable, and moreover saleable, heat and power. Gasification and pyrolysis technologies produced a range of moderate CV fuels, which could have a range of industrial uses if investigated further; the use of SMC is thus not limited to the direct

generation of heat and power, but has wider applications for other sectors of industry. The gaseous emissions were monitored and as these were not extreme – based on the WID guidelines, the gas cleaning required will be minimal. Particulate problems can be counteracted with suitable particle removal technologies. The AI of the ash means that SMC has only a moderate potential for fouling, which is lower than other biomasses, and is thus an advantage for the large-scale use of this source of energy; the lower the potential to foul, the less damage to the reactor and thus downtime can be minimised to only occasional repairs. The lower temperatures of a fluidised-bed would mean ash melting and agglomeration are also less likely. Including NaOH as a binder would increase the likelihood of these issues however.

From this, it is clear that these pellets can be utilised as a fuel for combustion. As the 200,000 t/a of SMC is widely distributed, small energy recovery facilities, perhaps at individual farms will be the best way to utilise this technology, to minimise transportation costs. Alternatively, where there are groups of farms (such as in the border region of Ireland), centralised power stations can make use of SMC from a wider area, providing heat and/or power to the farms or surrounding area. If other thermal treatments are used, these too could be carried out on a farm-to-farm basis, where the need for particular fuels arises.

Whilst the experiments performed here were on a laboratory scale, they have implications for the larger-scale use of such fuel pellets, as the results can be scaled up. This would primarily concern the bed-depth-to-diameter ratio of the fluidised-bed used. There would also be differences in the fluidising and bubbling behaviour between the different categories of particles, which would mean there can be large changes when scaling up from small systems to commercial operations, thus the use of a semi-industrial, fluidised-bed would greatly aid the further implementation of such fuels (Botterill, 1983).

11.3.2 Costs

Although the initial costs of the drying, pelletisation and thermal treatment equipment, such as a fluidised-bed, in addition to the gas cleaning equipment required may be high, the costs will eventually be offset by the energy gained from the sale of heat and/or power or the money that is saved from no longer having to purchase these. This pay-back is obviously dependent on various factors, such as the amount and method of drying, pelletisation pressure, thermal conversion technique employed and its efficiency, the degree of gas cleaning and the cost of other uses for SMC. As the drying costs were such a large proportion of overall expenditure, many factors would have to be considered to assess the viability of this process to see if such costs could be offset; this would include the fees charged for disposing of these materials. Additional costs may arise from transporting the wastes to a centralised plant, if they are not used *in situ*. Due to the renewable nature and CO_2-neutrality of the SMC, financial aid may be available for its use. Any apposite subsidies that could be acquired to assist the processing or use of the wastes may further offset the high processing costs to make these materials into a usable fuel product. Such funding or other forms of assistance may be applicable, based on the Climate Change Levy and the Non-Fossil Fuel Obligation.

11.3.3 Environmental Impacts

The emissions from these processes were monitored and the most harmful species, such as NOx and SOx, were found in insignificant concentrations; this means that vast amounts of expensive gas cleaning equipment should not be required if this process is to be used industrially, although technologies are available to control detrimental pollutant emissions. The environmental impact of this should therefore be minimal. Additionally, the ash from combustion was analysed and heavy metal concentrations were negligible, thus the ash can be reused as an activator for PFA, as previously described, eliminating the need for landfilling. It should also be considered that the use of SMC and coal tailings has a number of environmental benefits. Using this waste product from industry means that the SMC can be diverted from landfill and other environmentally-degrading disposal routes; furthermore, as SMC is a biomass and therefore a renewable energy source, it is CO_2-neutral and thus would not contribute to the enhanced greenhouse effect and its associated issues. The use of coal tailings ensures that contaminated land will be cleaned and reclaimed for public and/or private use.

11.3.4 Public Perception

The public perception and acceptance of alternative fuels is not necessarily good, particularly if it is seen as waste incineration; the 'NIMBY' effect may also be problematic if energy generation facilities are located in close proximity to residential areas. The aims of the operations and overall benefits of the process need to be highlighted and contrasted to the detrimental health and environmental effects of continuing to produce energy from unsustainable sources, such as coal. The current disposal methods of both wastes can be emphasized as environmentally-degrading, as well as SMC management being a barrier to the future development of the mushroom industry. The implementation of a viable disposal technique with energy recovery will thus be beneficial to the local economy, particularly if the energy recovery facility proposed is to be located at a mushroom farm.

11.4 ERROR ANALYSIS

There were three main sources of error concerned with the experimental and modelling phases of this work. Measures were taken to minimise the impacts of each. Firstly, there were systematic instrument errors, concerning such equipment as the gas analysers. Specific accuracies were given for each source of error, as considered in the experimental measurement accuracy sections throughout the experimental chapters. Through regular calibrations of these instruments and taking average readings from repeated testing, it was considered that these errors were significantly reduced.

Secondly, there were human errors concerning the data measurements. These were also minimised by repetition. For the material characterisation phase, several tests were completed and averages of the data were taken. This was principally necessary for this phase, as the SMC was quite heterogeneous. For the pelletisation phase, 5 pellets were made for each condition, in order to take a mean of the results. The

thermal treatments were also completed more than once, so averages of the key data, such as temperatures and gas concentrations, could be made.

Thirdly, there were errors with the theoretical side of the work, which concerned both the equations employed to analyse the data obtained, such as the pellet pile-up equations and the combustion efficiency calculations, and the modelling phase. Any errors in the data due to the instruments or human errors involved in their collection may have been augmented here, particularly if the data had been rounded or subsequent equations were utilised on data that had already been manipulated in some way. There were also errors concerned with the modelling work, as explored previously; any theoretical modelling or calculations, for example estimating the potential heat and power generation are likely to contain inaccuracies. The costings concerning the processing of these wastes were expected to contain significant errors, as assumptions were made and various quantities had to be estimated. The final figures, whilst somewhat erroneous are likely to give an indication of the magnitude of the overall costs.

11.5 PROJECT EVALUATION

In order to evaluate this project, the limitations need to be considered, with suggested improvements and recommendations. As with all research, a number of limitations apply and were present; through identifying these, the conclusions, the recommendations for further research and the applications of the work can be more valid and put to better use. There were many sources of error concerning the experimental results, which impact upon their validity; these include sampling error (as the SMC was fairly heterogeneous), human error, equipment error and those associated with data collection and manipulation. The largest of these errors is likely to be in the final results, as this will contain the accumulation of all previous errors, from the range of sources identified. These issues have been discussed previously, relating to each experimental chapter.

Based on these limitations, many things can be rectified, through identifying areas where improvements can take place. The primary limitation of this work is that further research is clearly required in all areas of experimentation this thesis has covered; specific recommendations for further and additional research into this field are presented in the following chapter. Improvements to the existing work would simply be the replication of such experiments, to ensure the validity and accuracy of the results. This would be most valuable for the pelletisation studies, where, due to time constraints, only 5 pellets could be made per condition and thus there was often significant variability in the results obtained. This was due to the heterogeneity of the materials, the SMC in particular. Whilst using such a small sample size for each test meant that a wide range of variables and conditions within could be compared, a larger number of pellets would have been beneficial in improving the significance of trends and highlighting further the difference or similarities between the test cases. The fluidised-bed combustion tests, whilst already repeated several times would also undoubtedly benefit from additional replications.

12

CONCLUSIONS AND FUTURE WORK

12.1 CONCLUSIONS

This work, concerning the reuse of two wastes – spent mushroom compost and coal tailings – for energy recovery, was conducted via extensive reviews of relevant literature and theoretical topics. Based on these, key experimental areas were identified: the characterisation and pelletisation of the materials and the utilisation of these in thermal treatment processes, including fixed- and fluidised-bed combustion, as well as gasification and pyrolysis. These experimental techniques were subsequently complimented with mathematical and theoretical modelling. The main conclusions from these are as follows:

- The material characterisation showed that the 'as received' moisture content of both the SMC and coal tailings were considerable. These high moisture contents (~40 % for the coal tailings and 66 % for the SMC) significantly reduced the CV and thus the potential energy that could be recovered. Drying is hence vital as these are to be used as fuels. The low density of the SMC means that pelletisation is also necessary prior to its utilisation as a fuel, to increase both the bulk and energy densities; controlling the moisture content for pelletisation would also be essential.

- The CV analysis of the materials determined herein was compared to those in the literature and was found to be commensurate for both. In accordance with this literature, both SMC layers had a lower NCV than the coal tailings – 13.33 MJ/kg and 11.71 MJ/kg for the substrate and casing in comparison to 19.22 MJ/kg for the coal tailings, on a dry basis. The high moisture and ash appreciably affected these values. The proximate analysis showed the majority of the energy content in the SMC was derived from volatile components, whereas for the coal tailings most was from fixed carbon.

- The other standard methods (ultimate and elemental analyses) identified elements that could be problematic to the thermal treatment of these fuels. These included noteworthy amounts of nitrogen, sulphur and chlorine, which could form acid gases; previous investigations, however, found that the majority of these elements remain as inorganic forms in the ash (Williams, 2001; Williams, *et al.*, 2001a; Chugh and Patwardhan, 2004). Whilst some chlorine was present in the SMC, the overall sulphur content may inhibit dioxin and furan formation (Fielder, 1998). Furthermore, it was thought that despite the significant sulphur content of the fuel, the high proportion of calcium in the SMC may act as a sorbent to minimise SOx formation, though phosphorous may impede this capture mechanism (Altun, *et al.*, 2006; Elled *et al.*, 2006). The high ash content suggests potential particulate problems and high particulate carryover if the particle sizes are small. The alkali metals, along with phosphorous, iron, silicon and aluminium were all found in the materials and if concentrated in the ash in oxide form after thermal treatment could increase the likelihood of slagging, fouling and ash agglomeration (Öhman, *et al.*, 2004; Fryda, *et al.*, 2006).

- From the literature review, key pelletisation parameters and methods for analysing pellet quality were identified. Of these the moisture content, pressure and composition had the most noticeable impacts on pellet properties; holding time however did not have such a substantial effect on any of the quality assessment criteria, which included density, tensile strength, pellet pile-up heights and durability. Optimum values were determined for each variable: a moisture content of 10-11 % at a pressure of 6000 psi (41.4 MPa) followed by complete air drying for a 50:50 wt% SMC-coal tailing ratio led to the formation of the best quality pellets. Such pellets had a net CV of 16.11 MJ/kg.

- Whilst the pellets made using these optimal conditions showed significant quality improvements, the product was still friable, producing dust on handling, transport and feeding. Maize-based starch and caustic soda were thus considered as organic and inorganic binders; 1 wt% of either enhanced pellet tensile strength, with starch having more pronounced effects. NaOH improved durability, though was later found to detrimentally-impact combustion.

- In addition to adding binders, inherent binders were also evaluated. As much of the SMC is composed of straw, it had a significant lignin and cellulose content, which would soften on heating to act as a binder. Both the use of elevated temperatures and steam conditioning were considered. Up to 75 °C improved all criteria used to assess pellet quality, although 45 °C appeared to be just as significant according to ANOVA tests. Additional heating (125 °C) did not further enhance pellet quality. Steam conditioning of the materials prior to pelletisation was also conducted using super-heated steam; 5 minutes of conditioning, whilst optimal, increased only the tensile strength of pellets.

- Based on the review of thermal treatments, combustion, gasification and pyrolysis were compared. In the preliminary tests, the raw SMC and 50:50 SMC-coal tailing pellets were combusted in a fluidised-bed and compared to their combustion in a fixed-/packed-bed. These were then contrasted with SMC gasification and pyrolysis. Pellet combustion performed better in both instances and the fluidised-bed

was also found to be more efficient. Whilst pyrolysis produced a range of fuels for subsequent use, their CV was low; gasification was not successful.

- As pellet combustion in a fluidised-bed was determined the most appropriate use for these wastes from the initial comparison, this was investigated in greater depth. Three principal operating parameters were identified and tested, from which optimal combustion conditions were established. These included a pellet feedrate of 3.25 kg/hr (180 kg/m^{2}hr) and a total air flowrate of 650 kg/m^{2}hr, where primary air was set at 480 kg/m^{2}hr; this resulted in an air ratio of 2.6. A bed depth of 0.22 m was also preferable. Such conditions would achieve good combustion efficiencies (~96 %), along with high temperatures in the bed (≥850 °C) and low pollutant concentrations (minimal CO and NOx). Acid gases were fairly negligible and generally conformed to the Waste Incineration Directive, although some gas cleaning would be needed. Particulate formation and thus flyash capture was considerable; highly efficient removal strategies will certainly be required. The ash analysis found that various species, such as K, Na, P, Si, Al and Fe were concentrated here and may contribute to slagging, fouling and ash agglomeration if in oxide form. Fortunately, the temperatures achieved with fluidised-bed combustion are considerably lower than the ash fusion temperatures noted herein, which indicates the suitability of this technology.

- Although high combustion efficiencies could be achieved using the optimised conditions, innate inefficiencies with the reactor meant that alterations could improve combustion. Scaling-up the reactor would mean a deeper bed could be employed whilst maintaining a relatively low bed depth-to-diameter ratio to enhance the overall efficiency. Modifying the experimental set-up by including an afterburner or staged, turbulent secondary air at suitable locations to aid freeboard mixing and redistribute the fuel and oxidiser could also be utilised to improve the combustion efficiency.

- As caustic soda and starch were considered as binding agents, their impact on combustion thus needed to be determined. It was discovered that 1 wt% of either did not greatly affect the temperature profile, however, their influence on gas concentrations was significant. More CO was present in both cases, reducing the combustion efficiency from 95.0 % to 88.0 %; acid gas species were not as ubiquitous in these cases. A small increase in the Alkali Index was noted where sodium was included in the fuel as the caustic soda binder. The ash fusion temperatures were approximately 50 °C lower for this sample than the control (where no binder was used) or where starch was the chosen binder.

- FLUENT was employed to replicate the experimental data concerning pellet combustion in a fluidised-bed. By manipulating various input parameters, a range of scenarios were modelled, which were compared to the corresponding empirical determinations of the temperature profiles and gas concentrations. Based on the modelled case that most closely imitated the experimental information, which had an average error of 3 % for temperatures prediction, particles were added at the base of the reactor to assess the transport disengagement height. It was found that bed particles, characterised by their size and density, would elutriate from the bed and be entrained in the upward primary air flow. They would however fall from the gas stream shortly after and return to the bed, not reaching the exit.

This suggested a sufficient freeboard height was provided and corroborates the experimental data, as sand particles were not found in the flyash collected in the cyclone. Flyash elutriation and removal via the exhaust duct was modelled and also supports the experimental evidence.

- By completing mass and energy balances based on the experimental data gained, potential heat and power generation were computed from the industrial-scale combustion of these wastes. Several cases were compared and it was found that over 5 MWe could be generated if 100,000 t/a of SMC (the amount that is thought to be available for energy recovery in the Irish border counties) was combusted with 100,000 t/a of coal tailings, assuming a process efficiency of 18.6 %.

- An economic analysis of the overall process was performed, based on the framework conditions of a plant scale of ~12,000 t/a of dried SMC-coal tailing pellets. The purchasing and transportation of wet fuels were found to be considerable, even for short haulage distances; for the scenario investigated, these combined are likely to total more than £30,000/a, for transporting 6000 tonnes of coal tailings 25 miles. As a mushroom farm was chosen as the processing facility, no SMC purchasing or transport costs were included. The initial investment costs, such as purchasing drying and pelletisation equipment, including facilities to cool and store the pellets, were also significant, around £900,000. The drying process for these high moisture content wastes was likely to total more than £250,000/a, which was £22.50/t of pellets produced, whilst the specific pelletisation and storage costs were thought to be £8.50/t. The direct cost of electricity produced would thus be about 3.5 p/kWhr.

- As both the SMC and coal tailings are waste materials, their combustion or other thermal treatment must conform to the Waste Incineration Directive. The laboratory-scale fluidised-bed combustion of these fuel pellets demonstrated that acid gas emissions – NOx, SOx and HCl – were unlikely to be problematic and would generally meet emissions limits, though on occasion, the concentrations were slightly above those outlined. Accordingly, some gas cleaning would be required to ensure this legislation is met. Particulate emissions were collected in vast quantities, thus highly efficient removal strategies would need to be employed to guarantee environmental safe-guarding.

12.2 RECOMMENDATIONS FOR FURTHER WORK

Based on the discussion of the results and the limitations of this research (in the previous chapter), in addition to the above conclusions, the following recommendations have been made with regard to the continuation of research in this field:

- Additional material characterisation studies of both the SMC and coal tailings may be favourable. Thermogravimetric analysis and differential thermograms could divulge information concerning the specific components contained within these materials. Lignin is however notoriously difficult to identify in such tests, though a range of others could be recognised using these methods.

- The main area of research that should be considered is pelletisation, specifically a larger-scale pelletiser and associated, integrated equipment for testing. Modifying the pelletisation process would

mean that a wider range of variables could be tested and the results more accurate, as a larger number of pellets could be manufactured and tested in the same amount of time. A mechanised pelletisation rig to enable better and more precise control over pelletisation parameters would greatly benefit such tests. A pelletiser with an integrated digital pressure gauge and a digital tensometer for compressive strength testing would minimise human error and thus reduce the subjective nature of these tests. Equipment for curing, drying and/or post-treating the pellets after manufacture would further profit such a specialised process. Facilities for standardised durability testing would also be greatly beneficial. Larger-scale apparatus would facilitate the comparison of such results to those of Temmerman, *et al.* (2004; 2006) and would be an excellent way in which to encourage the use of standard methods and processes in this field. It would therefore increase the likelihood that other institutions would also wish to adopt these methods.

- Further to this, additional binders that may be more effective should be evaluated, thus investigations into other suitable binders for these fuels would be beneficial. Only two binders were compared, in addition to those inherent to the fuels. Several other binders were identified in the literature review as apposite for such an application, as a range of biomass fuels were found to have been pelletised. Moreover, additional facilities to aid the combination of the material and a binder could be included into the extensive pelletisation set-up considered above.

- Larger-scale combustion tests, such as in a pilot-scale reactor would be advantageous. Scaling-up the reactor, as previously considered would enable a deeper bed for improved carbon burnout and thus the achievement of greater combustion efficiencies. The information that could be gained from such tests would benefit the industrial use of these wastes as fuel resources.

- Alternative options to combustion would be gasification and pyrolysis; additional tests would be required as those herein were only for demonstrative purposes. Although these proved successful in terms of the reactions that took place, more in-depth, advanced investigations are certainly necessary. An examination of these processes is needed under a variety of conditions to further demonstrate their potential. Gasification in particular will need to be reassessed, since the packed-bed tests were not successful, as the conditions were not appropriate. The use of a specifically designed gasification unit would therefore be required to explore this to a satisfactory extent. Utilising a gasifier for such a purpose would ensure apposite conditions prevailed in the reactor, including the use of pre-heated primary air, which would be enough to initiate and encourage gasification reactions, but not so much that combustion reactions predominate. Pyrolysis (thermal degradation) could also have been examined in greater detail. A range of fuel products were formed and by varying the conditions under which the pyrolyser was run, the product yields and compositions could have changed to maximise the formation of the highest CV products, as outlined in Table 3.2.

- This feasibility study indicates that electricity production from SMC-coal tailing pellets is potentially viable, especially if the waste heat is utilised. Detailed economic studies of the proposed process, including tax incentives, are therefore recommended.

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APPENDICES

APPENDIX A: INFORMATION DISSEMINATION

A1 List of Journal Publications

Ryu, C., **Finney, K.**, Sharifi, V. N. and Swithenbank, J. (2008) Pelletised fuel production from coal tailings and spent mushroom compost – Part I. Effect of pelletisation parameters, **Fuel Processing Technology**, Vol. 89, 269-275

Finney, K. N., Ryu, C., Sharifi, V. N. and Swithenbank, J. (2009) The re-use of spent mushroom compost and coal tailings for energy recovery: Comparison of thermal treatment technologies, **Bioresource Technology**, Vol. 100 (1), 310-315

Finney, K. N., Sharifi, V. N. and Swithenbank, J. (2009) Combustion of spent mushroom compost and coal tailing pellets in a fluidised bed, **Renewable Energy**, Vol. 34 (3), 860-868

Finney, K. N., Sharifi, V. N. and Swithenbank, J. (2009) Fuel pelletisation with a binder: Part I – Identification of a suitable binder for spent mushroom compost-coal tailing pellets, **Energy and Fuels**, Vol. 23 (6), 3195-3202

Finney, K. N., Sharifi, V. N. and Swithenbank, J. (2009) Fuel pelletisation with a binder: Part II – The impacts of binders on the combustion of spent mushroom compost-coal tailing pellets, **Energy and Fuels**, Vol. 23 (6), 3203-3210

A2 Conferences

WARMNET – Tackling Waste 2007, The School of Applied Sciences at The University of Northampton and The School of Chemical, Environmental & Mining Engineering at The University of Nottingham, Nottingham, U.K., Karen Finney as presenter of "The Reuse of Spent Mushroom Compost for Energy Recovery" (04/07/2007)

CIWM 2008 Conference, The 6th International Symposium on Waste Treatment Technologies, Paignton, U.K., Karen Finney as poster presenter of "The Reuse of Spent Mushroom Compost and Coal Tailings for Energy Recovery" (11/06/2008)

Environment Division Symposium, University of Sheffield, Sheffield, U.K., Karen Finney as presenter of "Generation of Green Energy from Mushroom Compost and Coal Tailings" (17/11/2008)

Bioenergy 2009, Jyväsklyä, Finland, Karen Finney as presenter of conference paper and poster of "The Reuse of Spent Mushroom Compost and Coal Tailings for Energy Recovery" (02/09/2009)

Joint Meeting of the Coal Research Forum, Environment Division and the Royal Society of Chemistry Energy Sector with the Energy Sector AGM, Seminar on Co-firing and Fuel Characterisation, University of Nottingham, Nottingham, U.K., Karen Finney as presenter of "The Reuse of Spent Mushroom Compost and Coal Tailings for Energy Recovery" (15/09/2009)

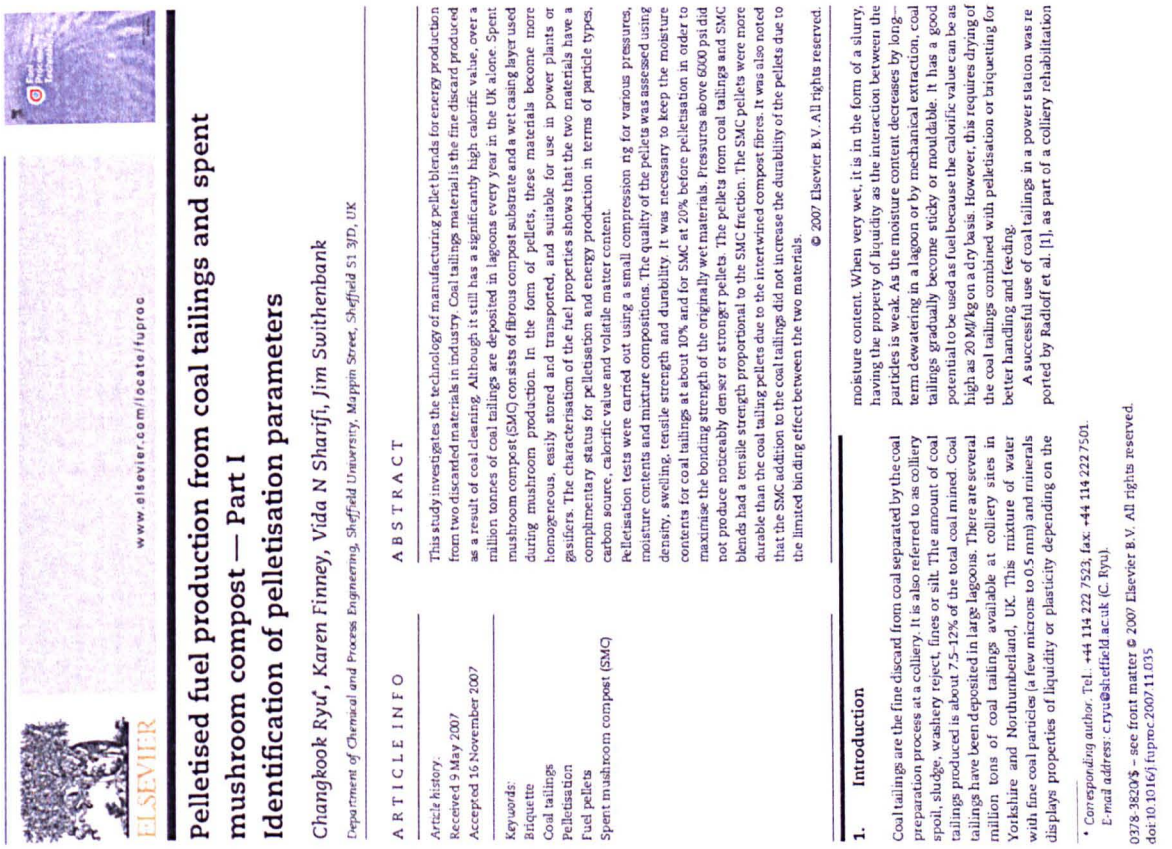
A3 Departmental Seminars and Events

Combustion and Incineration Group Meeting, Karen Finney as presenter of "The Reuse of Spent Mushroom Compost for Energy Recovery" (11/07/2007)

24-month Departmental Seminar, Karen Finney as poster presenter of "The Reuse of Spent Mushroom Compost and Coal Tailings for Energy Recovery" (27/10/2008)

30-month Departmental Seminar, Karen Finney as presenter of "The Reuse of Spent Mushroom Compost and Coal Tailings for Energy Recovery" (01/04/2009)

APPENDIX B: PUBLICATION 1 – FUEL PROCESSING TECHNOLOGY



FUEL PROCESSING TECHNOLOGY 89 (2008) 269–275

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Pelletised fuel production from coal tailings and spent mushroom compost — Part I

Identification of pelletisation parameters

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ABSTRACT

This study investigates the technology of manufacturing pellet blends for energy production from two discarded materials in industry. Coal tailings material is the fine discard produced as a result of coal cleaning. Although it still has a significantly high calorific value, over a million tonnes of coal tailings are deposited in lagoons every year in the UK alone. Spent mushroom compost (SMC) consists of fibrous compost substrate and a wet casing layer used during mushroom production. In the form of pellets, these materials become more homogeneous, easily stored and transported, and suitable for use in power plants or gasifiers. The characterisation of the fuel properties shows that the two materials have a complimentary status for pelletisation and energy production in terms of particle types, carbon source, calorific value and volatile matter content.

Pelletisation tests were carried out using a small compression rig for various pressures, moisture contents and mixture compositions. The quality of the pellets was assessed using density, swelling, tensile strength and durability. It was necessary to keep the moisture contents for coal tailings at about 10% and for SMC at 20% before pelletisation in order to maximise the bonding strength of the originally wet materials. Pressures above 6000 psi did not produce noticeably denser or stronger pellets. The pellets from coal tailings and SMC blends had a tensile strength proportional to the SMC fraction. The SMC pellets were more durable than the coal tailing pellets due to the intertwined compost fibres. It was also noted that the SMC addition to the coal tailings did not increase the durability of the pellets due to the limited binding effect between the two materials.

1. Introduction

Coal tailings are the fine discard from coal separated by the coal preparation process at a colliery. It is also referred to as colliery spoil, sludge, washery reject, fines or silt. The amount of coal tailings produced is about 7.5–12% of the total coal mined. Coal tailings have been deposited in large lagoons. There are several million tons of coal tailings available at colliery sites in Yorkshire and Northumberland, UK. This mixture of water with fine coal particles (a few microns to 0.5 mm) and minerals displays properties of liquidity or plasticity depending on the moisture content. When very wet, it is in the form of a slurry, having the property of liquidity as the interaction between the particles is weak. As the moisture content decreases by long-term dewatering in a lagoon or by mechanical extraction, coal tailings gradually become sticky or mouldable. It has a good potential to be used as fuel because the calorific value can be as high as 20 MJ/kg on a dry basis. However, this requires drying of the coal tailings combined with pelletisation or briquetting for better handling and feeding.

A successful use of coal tailings in a power station was reported by Radloff et al. [1], as part of a colliery rehabilitation

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project in Australia. In this scheme, 70 kt/yr of 50 mm diameter briquettes with 10–20% moisture content a were produced using a double roller press. The pellets were successfully burned at a local power station at a rate of up to 10% of fuel feed. However, the details of the briquetting conditions, binder used or the quality of the product were not presented in the above mentioned paper.

Any fibrous biomass materials can add more value to the pellets of coal tailings by increasing the pellet quality and carbon-neutral energy content. Yaman et al. [2] showed that some lignite and biomass blends increase the strength of the briquettes. The potential materials to be considered for mixing include straw and herbaceous energy crops; however, the present study focuses on fibrous biomass from an agricultural residue — the spent mushroom compost (SMC). The raw mushroom compost contains straw, poultry manure, horse manure and gypsum conditioned for about 3 weeks. Once compacted into about 6-inch thick substrate, the compost is covered by a 2-inch thick layer casing material that is a mixture of pure peat and chalk. After around 5 weeks of the mushroom production process, SMC is collected for disposal. The mushroom growing industry in the UK generates over 400 kt/yr of SMC. Some SMC is sold for horticultural purposes but the main disposal route is currently landfill or landscaping. A few other routes are available but there are environmental impacts such as eutrophication of watercourses. The use of SMC as fuel has been assessed in Ireland [3], but no actual work has been found in the literature on its use for fuel pellet manufacture or energy production.

By pelletisation, a raw material is converted into a value-added fuel with homogenous properties, shapes and sizes. This allows better handling, storage, transportation and feeding properties of the material. For bulky biomass such as sawdust and straw, pelletisation densifies the materials and reduces transportation cost. Pelletisation or briquetting of material is performed by applying pressure, shear or a combination of both. Among the many types of the pelletisers used in industry, the main categories are hydraulic presses, screw extruders, ring rollers, ring-dies and double rollers [4,5]. The common fuel pellets are coal briquettes, wood pellets and refuse-derived fuel.

Compared to the pelletisation of biomass and waste, the briquetting of coal for domestic and industrial uses is an old technology. The typical example is pillow-shaped charcoal for barbeques. Coal briquettes are produced from various types of coals typically by hot briquetting with the use of a binder. The common binders are coal tar, petroleum residue, sulphite liquor and starch [6]. Coal briquettes can be also produced by binderless briquetting at ambient temperature by applying high pressure alone [5]. This is more desirable in terms of production cost. Mangena et al. [7] investigated binderless briquetting of fine coals and suggested that the clay minerals particularly kaolinite may contribute to the bonding in the briquettes.

The bonding of particles in a pellet is determined by several mechanisms: van der Waal's force, liquid bridging force [8], particle interlocking [5] and, if used, high viscosity binder. In all of the above mechanisms, large contact areas between particles are essential to increase their cohesion strength. Under pressure, highly plastic particles easily deform to increase the contact area and to reduce the voidages. The plasticity of a particle is also affected by temperature (softening or thermal decomposition) and moisture content. Excessive moisture content increases the gap between particles and wastes the compression energy, while too low moisture content reduces the plasticity of the particles and increases the friction during pelletisation. Therefore, the main parameters become pressure, temperature, moisture content and mixture composition. Other factors include the particle size distribution and interweaving of fibres, if any, in a pellet. In the production of wood pellets, for example, the ideal moisture content is 10–15% which requires drying for wet materials [9]. No additives are used because lignin acts as a natural binding material which softens at elevated temperatures (~90 °C).

Pellets made from coal tailings and SMC are suitable for use in chain grate furnaces, industrial gasifiers or conventional pulverised fuel-based power stations where they can be fed into the mills. Fortunately, many mushroom farms are reasonably close to the colliery sites. SMC also contains lime which can help reduce sulphur emissions from coal combustion.

This paper presents the pelletisation properties of coal tailings, SMC and blends. The two basic materials were characterised for their physical, chemical and thermal properties. The pelletisation tests for the materials were carried out using a small compression pelletiser with a 1-inch diameter mould in order to identify the effects of process conditions such as pressure, moisture content and mixture composition. The pellet quality was assessed for density, swelling, tensile strength and durability.

2. Characterisation of SMC and coal tailings

Table 1 shows the results of standard fuel analysis of SMC and coal tailings. The raw SMC is very wet (moisture content of about 70%) and has a high ash content (34%dry). This leads to a very low net calorific value (1.6 MJ/kg — ar and 11.9 MJ/kg — dry). The volatile matter to fixed carbon ratio is about 4.5 which is lower than for typical biomass due to the presence of peat in the casing layer and the loss of some volatile matter during composting. The sulphur content is significant in SMC due to gypsum ($CaSO_4{\cdot}2H_2O$). However, sulphur in SMC is not

Table 1 – Fuel properties of SMC and coal tailings

Materials		SMC	Coal tailings
Moisture content (%ar)		~70	~40
Proximate analysis (%dry)	Volatile matter	53.57	25.07
	Fixed carbon	12.43	30.79
	Ash	34.00	44.14
Ultimate analysis (%dry)	C	39.86	47.87
	H	3.80	2.91
	N	2.12	1.01
	Cl	1.10	0.00
	S	0.62	1.38
	O (by difference)	18.50	2.69
Net calorific value	MJ/kg — dry	11.06	21.76
	MJ/kg — as received	~1.61	~12.08

Table 2 – Concentration of key elements in SMC and coal tailings

Element (ppm)	SMC	Coal tailings
Arsenic	0.5	10
Calcium	20,500	1860
Chromium	1	10
Copper	12.5	17.5
Iron	535	9300
Potassium	5500	1075
Magnesium	1720	2380
Manganese	64	113
Molybdenum	0.8	1.5
Sodium	1340	605
Phosphorous	1900	60
Lead	1.4	11
Antimony	9	<2
Zinc	50	30

expected to generate SOx during combustion since gypsum only decomposes at a very high temperature (1450 °C). Typical combustors operate below this temperature in order to avoid ash slagging and to protect the furnace. The typical particle size is 10–40 mm long fibres for the compost substrate and a few centimetres 'diameter' large aggregates of fine (50–800 μm) particles for the casing layer. The coal tailings are also very wet, with a moisture content that depends on the drying process undertaken at a colliery. As fine discard from coal cleaning, tailings have ash content above 40% on a dry basis. However, the calorific value is significantly high (about 22 MJ/kg—dry), which is comparable to wood pellets or refuse-derived fuel. The sulphur content is over 1%, which is typical for coal.

Table 2 lists the composition of trace elements in SMC and coal tailings. Ca is the most abundant in SMC due to gypsum and chalk ($CaCO_3$). Due to the biomass fractions in SMC, alkali metals (Na, K) also have high concentrations. Alkali metals may cause operational problems in energy recovery processes due to slagging and fouling of the heat exchanger surfaces due to the lowered melting point of ash. The concentration of phosphorous in SMC is also significant as it is one of key nutrients in the compost. Toxic heavy metals such as lead have very low concentrations in both materials.

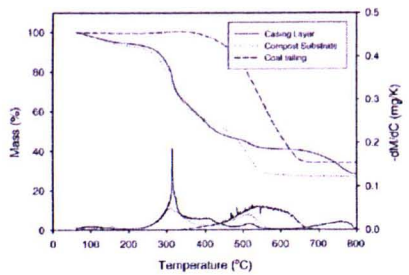

Fig. 1 – TGA curves of the samples.

Fig. 1 shows the thermogravimetric analysis (TGA) and differential thermogram (DTG) of air-dried SMC and coal tailings. The casing layer and the compost substrate of SMC were tested separately. The materials in SMC decomposed over two temperature ranges; 230–580 °C and 680–790 °C, respectively. The first range is attributable to the pyrolysis of lignocellulosic components. The peak on the DTG at 310 °C corresponds to the decomposition of hemicellulose [10]. The second range is due to the decomposition of chalk ($CaCO_3$) in the casing layer. With their low volatile matter content, coal tailings pyrolysed gradually between 350–670 °C with a broad peak of mass loss rate at 530 °C. The decomposition finished at 670 °C which was much higher than that for the organic components of SMC. This result is typical for coal.

3. Experimental methods

3.1. Pelletiser set-up

In order to assess the pelletisation parameters for SMC and coal tailings, a simple compression pelletiser was constructed using a hydraulic press as shown in Fig. 2. The pelletiser consists of a cylindrical mould (stainless steel, 150 mm long×26.8 mm ID) for material feeding and a ram for compaction seated on a hydraulic press. The ram is attached on the movable bottom plate, while the mould is fixed below the top plate. The mould is heated by two rope heaters (OMEGA FGR-060, 250 W each) with a K-type thermocouple connected to a temperature controller. It can compress the materials at various temperatures (up to 300 °C) and pressures (up to 10,000 psi).

3.2. Test conditions

The key parameters to be investigated were the moisture content pressure and temperature for each material or their mixtures Table 3 lists the pelletisation conditions tested. The moistur

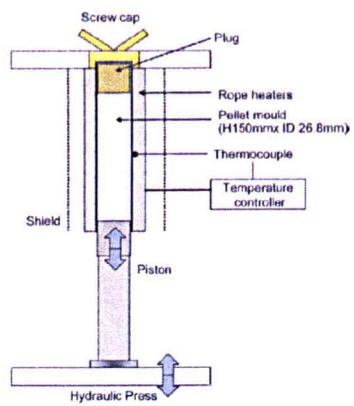

Fig. 2 – Schematic of the compression pelletiser.

Table 3 – Test conditions for pelletisation of SMC and coal tailings

Materials	Initial moisture content (%)	Pressure (psi)	Test parameters
Coal tailings	1–22	2440	Moisture content
Coal tailings	15	2440	Drying after pelletisation
Coal tailings	~10	810–7300	Pressure/drying after pelletisation
SMC	17–32	2440	Moisture content
Coal tailings: (SMC=5:5, (6:4, 7:3, 8:2, 9:1	~10	2440	Mixture composition

content was varied from 1 to 22% for coal tailings and 17–32% for SMC. The pelletisation pressure ranged from 810 to 7300 psi. For each test condition, 5 pellets were produced, each weighing about 10 g for SMC or 35 g for coal tailings. The length and weight of each pellet were recorded immediately after pelletisation and after air-drying. The pellets were 20 mm to 45 mm long, depending on the material and the process parameters.

3.3. *Assessment of pellet qualities*

In order to assess the quality of a pellet, the following five physical properties were used.

- Density, ρ (kg/m^3) = $W/(\pi DL)$
- Moisture content, M (%): measured after air-drying.
- Swelling, S (%) = $(L_2 - L_1)/L_1 \times 100 = [(\rho_1 v_1/\rho_2)/(W_1/W_2) - 1] \times 100$
- Tensile strength by the Brazilian test, σ (Pa) = $2F/(\pi DL)$
- Durability (%) = $W_2/W_1 \times 100$

where D: pellet diameter (0.0268 m), F: force from a tensometer (N), L: pellet length (m), W: pellet weight, 1: initial, 2: final.

The density of a pellet can be calculated from its dimensions and weight. The tensile strength was tested by a Monsanto tensometer, as a measure of cohesion strength between particles in the pellet. A pellet had two modes of deformation at the maximum pressure: fracture or deformation to an oval shape. When a pellet is made of fine particles, a crack develops and the pellet breaks into a few pieces. When a pellet contains intertwined fibres such as SMC or grass, the cross section becomes oval while remaining integrated. Together with the average values of the properties for 5 pellets, their variations were analysed to yield a 95% confidence limit.

The durability represents the resistance of a pellet to shock and wear during handling, transportation and feeding. In this study, the durability was measured for 5 pellets using a rotating drum (diameter 14.5 cm, width 6.5 cm) with one 1 cm high baffle across the sidewall. The pellets experienced consistent mechanical shock for every rotation due to the presence of the baffle, together with constant abrasion between pellets and by the drum. After 10 min of rotation at 40 rpm, the mass of the pieces larger than 2 cm (M_2) was weighed and compared to the initial mass (M_1). This test is based on the concept of the standard method for pellets proposed by CEN/TC (Commission European de Normalisation/Technical Committee) 335 on solid biofuels [11]. The standard method requires a 300 × 300 × 125 mm tumbling device with an internal baffle, which is too large for a lab-scale test as in this study.

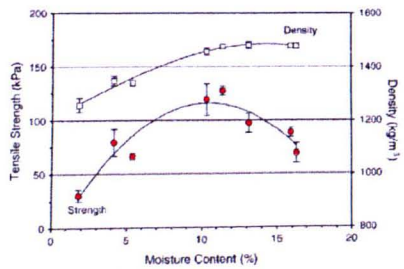

Fig. 3 – The effect of initial moisture content to the pellet quality (pressure: 2440 psi, tested immediately after pelletisation).

4. Results and discussion

4.1. *Coal tailing pellets*

4.1.1. *Effect of moisture content and pellet drying*

Fig. 3 shows the effect of moisture content on the pellet properties. The pellet density and strength were measured immediately after pelletisation. The moisture content of the sample prior to pelletisation greatly affected the strength of the pellet. The pellets from fully dried samples had the lowest density and tensile strength. Dry particles become hard while losing the plasticity, which increases the friction between particles that partially consumes the compression energy applied. The friction with the pellet mould also made the surface of the pellets shiny, unlike the pellets from wet coal tailings. These pellets were also very brittle — small chips and/or powders easily disintegrated from the pellet. The pellets from wet coal (over 13% of moisture content) also had much lower tensile strength. In wet coal tailings or slurry, the voids filled with water loosened the cohesion of particles while wasting the compression energy. Although the wetter pellets were denser (up to 1481 kg/m^3), the density after the pellets were dried was lower than the pellets of 10% initial moisture content. The tensile strength peaked to 120–128 kPa at 10–12% moisture content.

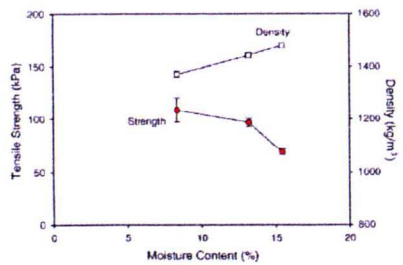

Fig. 4 – The effect of pellet drying on its density and tensile strength (pressure: 2440 psi).

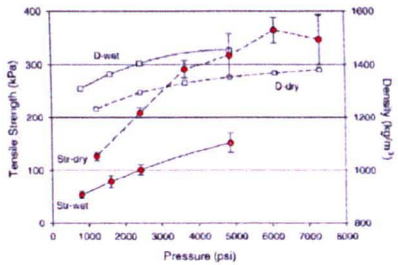

Fig. 5 – Effect of pressure on wet and oven dried coal tailing pellets (initial moisture content: ~9%, wet: tested immediately after pelletisation, dry: air-dried).

Fig. 4 shows the effect of pellet drying on tensile strength. While the moisture was essential to make a particle plastic and to reduce friction, it also made the pellets weak to deformation. The tensile strength increased to 115 kPa when dried to 8.3% moisture content from 73 kPa at 15% initial moisture content. As the shrinkage of the pellets was less than 1%, the density lowered solely by the moisture driven off. These results show that drying of the pellets as well as the control of the initial moisture content are both important.

4.1.2. *Effect of pressure*

Fig. 5 shows the effect of pressure on coal tailing pellets. The coal tailing pellets were prepared with an initial moisture content of about 9.0–9.6% and tested for density and strength immediately after pelletisation for pressures up to 4870 psi. The pellets produced at pressures up to 7300 psi were also tested after being kept in a dry place for 3 days. The final moisture content of the pellets after drying was 2.2%. Both the pellet density and strength increased as the pressure increased. At higher pressures, the density increase became smaller. This is because the initial compaction by rearranging particles to fill up the free interstices requires low compression energy and further increase in density by deformation or breakdown of particles requires high compression energy ([5], p. 65). The slight increase in density in the later stage (at high pressures), i.e., less air voids and larger contact area between particles, resulted in a continuous increase in the cohesion strength of the particles.

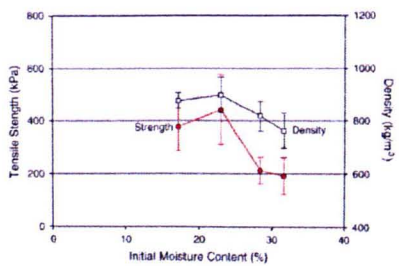

Fig. 6 – Effect of initial moisture content on SMC pellets (pressure: 2440 psi, tested for air-dried pellets).

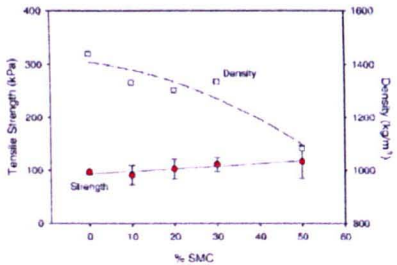

Fig. 7 – Properties of pellets from SMC/Coal tailings mixture (pressure: 2440 psi, initial moisture content: ~10%, tested for wet pellets).

When the pellets were fully air-dried, the tensile strength was doubled up to 364 kPa (Fig. 5). The final moisture content was 2.2%. The variation in the tensile strength also significantly increased, especially for the pellets at higher pressures. The drying also lowered the pellet density to a range of 1233 to 1380 kg/m^3 for pressures from 1220 to 7300 psi. These results are consistent with the of of pellet drying tests shown in Fig. 4.

The ideal pressure for pelletisation will depend on the pellet production cost and the required pellet properties including durability and strength. Commercial pelletisers or briquetting machines are capable of producing a pressure from a few thousands to over 30,000 psi [4]. Fig. 5 shows that pressures above 6000 psi do not have significant benefits. In terms of tensile strength, the above pressure can produce good quality pellets. The tensile strength represents the degree of particle cohesion resisting the compression force that pushes the pellet apart. A tensile strength of 291 kPa from a pressure of 3650 psi in Fig. 5 corresponds to 37.5 kg of 3 cm-long pellets with a density of 1330 kg/m^3 (367.5 N). Therefore, each pellet can sustain a pile of 1666 pellets (a height of 44.6 m) without fracture. The assessment of pellet durability will be presented later.

Table 4 – Durability of pellets tested using a rotating drum

Pellet type	Pelletisation conditions	Durability (%) after 10 min test
Wood pellet		98.8
Straw (air-dried, ~5 cm long fibres)	2436 psi	98.9
Coal tailings	1218 psi, air-dried	66.8
"	2436 psi, air-dried	79.7
SMC	2436 psi, air-dried	93.0
"	4872 psi, air-dried	98.3
SMC:Coal tailings=2:8	2436 psi, air-dried	79.1
SMC:Coal tailings=5:5	2436 psi, air-dried	71.1

4.2. Blends of coal tailings and SMC

The pelletisation of SMC alone is not very attractive compared to other biomass materials due to its low calorific value and the increase in the production costs required for drying such wet materials. However, the effect of moisture content on the raw SMC pellets was investigated as shown in Fig. 6. The moisture content ranged between 17–32% before pelletisation and 10.6–14.1% after air-drying. The density was up to 897 kg/m^3, which was significantly lower than that of the coal tailing pellets (1295 kg/m^3 at 2440 psi in Fig. 5). Apart from the lower particle density of the SMC fibres, the swelling was the main reason for such low densities. The pellets with an initial moisture content of 17% swelled by 7.1% while those with 32% initial moisture content swelled by 20.9%. The swelling has also been reported for the pellets of herbaceous crops [12]. During drying, the wetter pellets developed more cracks and distortion, which shows a lower degree of bonding and results in a lower tensile strength (about 200 kPa). Compared to the coal tailing pellets, the SMC pellets with 17% and 23% of initial moisture content had much higher tensile strength (376–441 kPa). The entwined fibres in a pellet could distribute the compression force better and, when deformed at the maximum force, the pellet became oval rather than fractured unlike the coal tailing pellets. Fig. 6 also shows that the variations in density and tensile strength were much higher than those for coal tailing pellets, which is attributable to uneven mixing of the SMC ingredients (the powdery casing layer and the fibrous compost substrate).

Fig. 7 shows the properties of the pellets from coal tailings and SMC blends. Both samples had about 10% moisture content before pelletisation. Although the tensile strength gradually increased to 125 kPa with a 50% SMC fraction from 100 kPa for coal tailing only pellets, this was not enough to compensate for the decrease in the pellet density as well as in the calorific value.

4.3. Durability of pellets

Table 4 lists the durability of the pellets tested for key cases together with the comparable test results for wood and straw pellets. The moisture content of coal tailings and SMC was about 10% and 20%, respectively, before pelletisation. The wood pellets (8 mm in diameter) produced by BrikettEnergi, Sweden, showed a very high durability due to the binding effect of lignin at elevated temperatures during the pellet production. Here, the straw pellets were manufactured by using the pelletiser at room temperature for the test. These pellets were also very durable due to the intertwined fibres that keep the pellet integrated. The SMC pellets were as durable as the wood or straw pellets when produced at a high pressure (4872 psi). However, the pellets of coal tailings and their mixtures with SMC were significantly less durable. During the tests, the edges of the cylindrical coal tailing pellets gradually eroded when they were exposed to wear and shock. The SMC added to the coal tailings lowered the durability of the pellets because the binding between the SMC fibres and the coal tailing particles was not strong enough. The blended pellets disintegrated first into large pieces and further into small pieces or powder during the tests. The use of special binders could be considered if the durability of the pellets needs to be increased in order to meet any requirement for a market outlet.

5. Conclusions

The fuel properties of coal tailings and SMC were characterised and their pelletisation properties were investigated for key process parameters using a simple compression rig. The raw SMC had a moisture content of about 70% with a net calorific value of about 11 MJ/kg on a dry basis. Coal tailings had a calorific value of about 22 MJ/kg on a dry basis.

For both materials, the quality of the pellets was significantly influenced by the moisture content. The optimum moisture content for pelletisation of coal tailings was about 10%, which produced pellets with a density of up to 1380 kg/m^3 and a tensile strength of up to 364 kPa. The ideal moisture content for SMC pellets was about 20%. The drier or wetter materials produced pellets with significantly lower compressive strength. The drying of pellets was also essential since air-dried pellets were twice as strong. No significant increase in density and strength was found for pressures above 6000 psi.

The addition of SMC to coal tailings slightly increased the tensile strength but reduced the density and the calorific value of the pellets. The changes in the pellet strength were proportional to the SMC fraction in the mixture while no increase was found in the durability of the pellets. The results suggested that there is no significant benefit of SMC addition in terms of pellet quality. However, the addition of SMC has other benefits such as greenhouse gas neutral energy production and potential capture of SO_2 by lime in SMC [13]. The use of binders needs to be investigated further in order to produce stronger and more durable pellets.

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The reuse of spent mushroom compost and coal tailings for energy recovery: Comparison of thermal treatment technologies

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ABSTRACT

Thermal treatment technologies were compared to determine an appropriate method of recovering energy from two wastes – spent mushroom compost and coal tailings. The raw compost and pellets of these wastes were combusted in a fluidised-bed and a packed-bed, and contrasted to pyrolysis and gasification. Quantitative combustion parameters were compared to assess the differences in efficiency between the technologies. Fluidised-bed combustion was more efficient than the packed-bed in both instances and pellet combustion was superior to that of the compost alone. Acid gas emissions (NO_x, SO_x and HCl) were minimal for the fluidised-bed, thus little gas cleaning would be required. The fuels' high ash content (34%) also suggests fluidised-bed combustion would be preferred. The Alkali Index of the ash indicates the possibility of fouling/slagging within the system, caused by the presence of alkali metal oxides. Pyrolysis produced a range of low-calorific value-products, while gasification was not successful.

1. Introduction

To mitigate the impacts of our growing demand for energy and the increase in waste production, it is possible to use many wastes as fuel resources – two of these wastes include spent mushroom compost, hereinafter SMC, and coal tailings.

The formation of the mushroom compost substrate takes place in stages: (i) pre-wetting and mixing of straw, gypsum, horse manure, poultry litter, peat, lime and activators; (ii) phase I composting in windrows and bunkers; and (iii) phase 2 composting involving pasteurisation and conditioning. After this, a peat casing layer is added to the surface for mushroom cultivation (spawning, casing, pinning and cropping), after which it is cooked out and discarded (DEFRA, 2006; Iiyama et al., 1994). Disposal is problematic, unsustainable and harmful to the environment, since the majority goes to landfill or is used as agricultural fertilisers, where leaching can be a serious issue for local water courses from both sources, as phosphorous and nitrates cause eutrophication. For every 1 kg of mushrooms grown, approximately 5 kg of SMC is produced. The generation rate of SMC is about 200,000 tonnes/annum in UK alone. The lack of sustainable waste management solution for SMC is the most significant barrier to the future development of this industry.

Previous studies into the use of SMC as a renewable fuel propose that SMC can be combusted in a bubbling fluidised-bed to generate power with high efficiency (McCahey et al., 2003; Williams, 2001; Williams et al., 2001; BioMatNet, 2004). The calorific value (CV) is comparable to other fuels, though drying or mixing with drier materials is needed. 'Auxiliary fuels', such as natural gas, can be co-fried with SMC to promote drying and enable greater energy recovery. Combustion of SMC leads to the production of ash, usually about 10% of its original volume, in addition to what it already contains. A preliminary investigation has been completed into the reuse of this ash as a chemical activator to enhance the pozzolanic reactivity of pulverised fuel ash (PFA) in the cement industry (Russell et al., 2005). SMC ash and PFA mixtures ensure rapid early improvements in the strength, although it is too soon to investigate the long-term implications of its use.

There are also many potential agricultural, horticultural and industrial uses of SMC including: An agricultural fertiliser (Gent et al., 1998; McCahey et al., 2003; Rhoads and Olson, 1995); a ruminant feed for sheep (Fazaeli and Masoodi, 2006); environmental enrichment in intensive pig farms (Beattie et al., 2001); treatment for coal mine drainage (Stark et al., 1994); bioremediation (Lau et al., 2003); enzyme extraction (Ball and Jackson, 1995); and a novel biosorbent (Chen et al., 2005).

Coal tailings are formed from coal cleaning processes, where coal is separated from its impurities. It has a significant proportion of moisture, although dewatering takes place in the lagoons where it is deposited, usually located in close proximity to the mining area. Lagoon management is vitally important, as mismanagement of these sites can result in contamination or lagoon failure, thus removing coal tailing deposits will eliminate these risks (Thompson, 1982). There are currently few uses of coal tailings. Noble and Dobrovin-Pennington (2005) investigated how it replace some

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Nomenclature

1	SMC-coal tailing pellets
2	raw SMC
AI	Alkali Index
BR	burning rate
Cb	cardboard
Cl^-	chlorides
CV	calorific value
FB	fluidised-bed
IFS	ignition front speed
IR	ignition rate
Mp	Miscanthus pellets
NO_x	oxides of nitrogen
P	pyrolysis
PB	packed-bed
Pc	pine cubes
PFA	pulverised fuel ash
RDF	refuse-derived fuel
SMC	spent mushroom compost
Sp	switchgrass pellets
Sr	raw switchgrass
SO_x	oxides of sulphur
SO_4^-	sulphates
Ww	willow wood

Greek symbols

ΔM	mass loss
η_{cc}	combustion efficiency
λ	equivalence ratio
ρ	density

Subscripts

C	char combustion stage
I	ignition propagation stage

of the peat in the casing layer added to the mushroom substrate, whereas Tiwari et al. (2004) focussed on its reuse for aggregates or the production of concrete blocks for construction. Only a few have examined its potential as a fuel, such as Chugh and Patwardhan (2004) and Radloff et al. (2004). The latter considered the processes of turning 70,000 tonnes/annum of waste from the Wallerawang colliery into fuel for a power station. This could be the greatest potential use of this waste, where 50 mm-diameter pellets were formed with a binding agent, followed by drying and then combustion with coarse waste from the coal mining industry.

There is a clear potential to combine these wastes, for energy recovery through use in thermal treatment technologies. Combustion, gasification and pyrolysis have been utilised with both conventional and renewable fuels to produce heat, energy and subsequent fuel products. These three treatments were compared herein, with the aim of determining the most appropriate technology for the reuse of SMC and coal tailings. Consequently, it is hoped that this will provide a renewable fuel for industry, divert SMC from landfill and aid the cleaning and reclamation of land contaminated by coal tailings. Furthermore, this may partially mitigate the impacts of environmental issues associated with present energy production and waste management strategies.

2. Methods

2.1. Characterisation of spent mushroom compost and coal tailings

Table 1 shows the material characterisation. The results for the SMC were comparable to those previously reported in the literature (Williams et al., 2001). The two SMC layers were quite analogous and the volatile and fixed carbon contents were similar to other types of biomass used for energy recovery. The nitrogen and sulphur contents were high, however it has been found from previous literature that these are mainly bound in inorganic forms (nitrates and sulphates), and thus fluidised-bed combustion will minimise the risks of forming NO_x and SO_x (Williams et al., 2001). All three substances have significant quantities of moisture and ash, which have detrimental implications on the CVs, as shown in Table 1. These were comparable to other wastes currently used as fuels, such as MSW and sewage sludge. Coal tailings have a comparable CV to sub-bituminous C coal and the other coal tailing samples (Radloff et al., 2004).

Table 1
Material characterisation of the coal tailings and the two layers of the SMC

Analysis	Constituent	Basis	Coal tailings	SMC substrate	SMC casing
Moisture (%)		ar	~40	65.70	68.56
Proximate analysis (%)	Ash	dry	41.25	26.89	28.87
	Volatile		20.51	61.80	60.18
	Fixed Carbon		38.24	11.31	10.95
Ultimate analysis (%)	Carbon	dry	47.87	35.13	35.72
	Hydrogen		2.90	3.59	3.01
	Nitrogen		1.01	2.85	1.11
	Chlorine		–	0.51	0.70
	Sulphur		1.38	2.95	2.16
CV (MJ/kg)	GCV	dry	19.85	14.11	12.37
	GCV	ar	11.91	4.94	4.33
	NCV	dry	19.22	13.33	11.71
	NCV	ar	10.55	3.08	2.51

Table 2 shows the full elemental analyses. In addition to the potential pollutants described above, other issues may arise due to the presence of specific elements. Slagging/fouling may occur due to the alkali metals present, specifically potassium and sodium. The large proportion of calcium, particularly in the SMC casing may be beneficial, however, as this could reduce SO_x compounds

Table 2
Selected results from the full elemental analyses

Element (mg/kg)	Coal tailings	SMC substrate	SMC casing
Al	4360.0	441.5	1435.0
As	14.8	<1	<1
Ca	2940.0	40600.0	118500.0
Cr	13.0	3.8	6.2
Cu	19.0	46.1	11.7
Fe	9700.0	1240.0	2580.0
K	1070.0	18650.0	3685.0
Mg	2420.0	4620.0	4265.0
Mo	2.3	4.1	0.3
Na	450.0	2095.0	600.0
P	74.3	6655.0	4220.0
Pb	12.9	2.6	5.1
Si	1380.0	1620.0	1485.0
Zn	34.6	194.5	64.1

in a similar manner to scrubbing processes – the sulphur content of all three components was quite significant. This sulphur can inhibit *de Novo Synthesis*, preventing the formation of dioxins and furans, as chlorine was also present in the SMC layers (Fielder, 1998). Iron and phosphorus were found in significant quantities, although heavy metals were not prevalent.

2.2. Spent mushroom compost and coal tailing pelletisation

Optimum values were experimentally-determined for a number of key pelletisation variables. The parameters included the moisture content (10–11%) followed by air-drying, compaction pressure (up to 6000 psi) and pellet composition (50:50 SMC:coal tailings wt% ratio). Pellet quality was based on their density, tensile strength, durability and maximum pellet pile heights (Table 3). The methods and results for these are presented in a previous publication (Ryu et al., 2008).

2.3. Methods for thermal treatments

2.3.1. Fluidised-bed for combustion

A small-scale fluidised-bed was used to combust the pellets (FB1) and the raw SMC (FB2). The fuel was placed in the sealed hopper of the calibrated pneumatic screw feeder. The sand on the perforated distributor plate 200 mm from the base of the reactor forms the fluidised-bed within the 2.3 m × 0.15 m stainless steel combustion chamber. This was heated with propane until the temperatures were stable, monitored using K-type mineral insulated thermocouples. Once this was achieved, the fuel was gradually fed in and the feedrate increased as the propane flowrate decreased. Table 4 shows the conditions for these and the subsequent tests. The exhaust produced passed through the cyclone to remove and collect particulate matter and the remaining gas was analysed for CO_2, CO and O_2 with an ADC MGA300 gas analyser, and NO_x (NO and NO_2) using a Signal Series 4000 NO_x analyser before being discharged to the atmosphere. Chlorides (Cl^-) and sulphate (SO_4^{2-}) species were collected by a wet chemical method, to indicate the presence of HCl and SO_x.

2.3.2. Packed-bed for combustion and gasification

A packed-bed was also used to combust the pellets (PB1) and SMC (PB2), as well as perform the gasification of the SMC. The fuel was placed onto the perforated grate at the bottom of the 1.5 m × 0.2 m reactor chamber and ignited using a gas burner. Primary and secondary air was fed from the bottom and top, respectively. Table 4 shows the operating conditions. The reactor was suspended from a weighing beam to monitor weight-loss during the reaction. The emissions passed through a probe to the cooling tower, where the moisture was condensed out before CO_2, CO and O_2 concentrations were established.

Table 3
Results of pellet density, tensile and compressive strengths and pellet pile-up

Variables and parameters	Optimum	1	2	3	4	5
Initial moisture content (%)	~15	16.3	16.0	~10	~15	~15
Drying	Yes	No	Yes	Yes	Yes	Yes
Pressure (psi)	2700	2700	2700	6000	2700	2700
Composition (SMC:coal tailings)	50:50	0:100	0:100	0:100	100:0	Substrate
Pellet diameter (mm)	26.8	26.8	26.8	26.8	26.8	26.8
Pellet length (mm)	43.0	31.8	32.0	4.3	56.7	5.8
Density (kg/m^3)	1083.7	1483.3	1371.0	1387.9	661.4	689.7
Tensile strength (kPa)	116.4	69.4	108.7	364.1	60.8	179.1
Compressive strength (N)	134.3	59.1	91.2	421.7	92.5	277.1
Weight (kg)	11.9	7.1	9.5	43.0	9.4	28.3
Number of pellets	451.7	266.1	384.4	1290.4	445.9	1258.7
Height of pellet pile (m)	12.10	7.13	10.30	34.58	11.95	33.73

1: wet coal tailings; 2: dried coal tailings; 3: coal tailings at high pressure; 4: SMC and 5: SMC substrate.

Table 4
Thermal treatment conditions and results for key parameters for the combustion tests

Parameter		FB1	FB2	PB1	PB2
Material		Small pellets	SMC	Large pellets	SMC
Amount of material (kg)		4.6	3.0	6.26	4.34
Primary air (kg/m^{2}h)		240–610	190–770	720–1200	720
Secondary air (kg/m^{2}h)		60–90	90	480	0–480
Average gas Concentration	CO_2 (%)	13.50	12.91	17.28	17.19
	O_2 (%)	4.22	4.04	0.49	2.76
	CO (%)	1.22	1.38	1.85	5.22
Combustion efficiency, η_{CE} (%)		91.7	90.3	90.3	76.7
Average Temperature (°C)	Bed	816	799	1139	1133
	Above bed	813	797	1117	728
	Freeboard	509	443	1055	735

2.3.3. Pyrolyser

Pyrolysis (P) was performed in an electrically-heated, insulated 130 mm × 320 mm stainless steel chamber, where the SMC was placed in the primary fixed-bed at the top of the cylinder. During the reaction, char was formed, which remained inside the reactor. This was fed with nitrogen at the base to prevent oxidation and to force the volatiles into the subsequent analysing equipment. These volatiles passed through a heated tube and were condensed to collect pyrolytic liquids. The gases were fed through a condensing tower, where samples were taken to assess the changing syngas (gaseous fuel product) composition with temperature. These were analysed with a Varian CP 3000 gas chromatograph. The exhaust then entered the CO_2 and CO analyser. The solid, liquid and gaseous fuels were analysed for composition and CV, as appropriate.

2.4. Further data analysis

Based on the CO and CO_2 concentrations, the combustion efficiency (η_{CE}) was calculated for the combustion cases. A number of other quantitative combustion parameters, namely mass loss (ΔM), ignition front speed (IFS), ignition rate (IR), burning rates for ignition propagation and char combustion (BR_I and BR_C) and equivalence ratio (λ) were determined for the packed-bed cases to evaluate their performance (Ryu et al., 2006, 2007a; Ryu et al., 2007b). The Alkali Index (AI) was computed to assess the potential for slagging/fouling. Values above 0.34 suggest fouling is certain (Jenkins et al., 1998). Full elemental analyses of the ash aided the determination of this parameter.

3. Results and discussion

The operating conditions used in the fluidised-bed and packed-bed cases and the key results are shown in Table 4. η_{CE} in the fluidised-bed was superior in the both cases and pellet combustion efficiency was also notably higher compared to the SMC alone. SMC pyrolysis produced a variety of low-CV fuels. These results are discussed below, although as SMC gasification was not successful, it is not considered further.

3.1. Combustion in the fluidised-bed

The combustion of the SMC-coal tailing pellets in the fluidised-bed (FB1) achieved the highest η_{CE} (91.7%) and was superior to the combustion of SMC (FB2). The gas concentrations were similar for both tests, although there was slightly more oxygen for SMC combustion, indicating fuel lean conditions, which resulted in a slightly lower efficiency (90.3%). The average NO_x concentration during pellet combustion was low (8.8 ppm ± 0.76), thus little gas cleaning, for example selective catalytic or non-catalytic reduction, would be required. Furthermore, SO_4^{2-} and Cl^- concentrations were 0.52 and 0.61 ppm, respectively, indicating the presence of SO_x and HCl species were also minimal. The Ca present in the SMC may have reduced some SO_x species, via the mechanism described above. Previous thermal treatments of SMC have shown that NO_x and SO_x will be negligible if it is combusted in a fluidised-bed, due to the inorganic origin of the majority of nitrogen and sulphur (Williams et al., 2001). It was also reported that though some HCl may form, most Cl should remain as chlorides in the ash (Williams et al., 2001; Williams, 2001). Additionally, it has been suggested that NO_x and SO_x emissions from coal tailing combustion would also be minimal (Chugh and Patwardhan, 2004). These findings were corroborated here. Temperatures for FB2 were somewhat lower than that for FB1, due to the inferior CV of the SMC. Temperatures in and just above the bed were higher than those in the freeboard in both cases.

3.2. Combustion in the packed-bed

The temperatures achieved during combustion in the packed-bed were higher than those in the fluidised-bed. The temperatures in the bed for PB2 were similar to those for PB1, although the freeboard was appreciably cooler. As the temperatures were significantly lower, there was less sintering off the ash for PB2. The O_2 concentration decreased to lower levels than that in the fluidised-bed and consequently, the combustion products (CO and CO_2) were more abundant, particularly CO, indicating less efficient combustion. η_{CE} for PB1 and PB2 were 90.3% and 76.7%, respectively, where the latter was severely affected by the high CO. It was found that the air flowrates were crucial in determining whether or not the fuel would burn, particularly for the SMC. If the air flowrates were too high, this caused dramatic cooling of the reaction and combustion ceased, whereas when the flowrates were too low, there was insufficient oxygen for the reaction to continue.

A range of quantitative combustion parameters were calculated (Table 5) and compared to those from the literature for miscanthus pellets (Mp), pine cubes (Pc), willow wood (Ww) and refuse-derived fuel pellets (RDF) (Ryu et al., 2006), cardboard (Cb) (Ryu et al., 2007b), switchgrass pellets (Sp) and raw switchgrass (Sr) (Gilbert et al., 2006). In general, these results corroborate well with other biomass combustion tests. ΔM_I was greater for the pellets compared to the SMC, and as such, the BR during this phase was much higher. By contrast, the BR during char combustion was more rapid for the SMC, although the overall BR was faster for the pellets. The IFS and IR for the pellets were both significantly lower than that for the SMC, due to the differential densities. Variations between the pelletised and non-pelletised fuels in this study have been confirmed by the differences between pelletised and non-pelletised switchgrass, namely ΔM_I, IFS and IR (Gilbert et al., 2006). ΔM_I was significantly lower for these tests, where the majority of mass loss occurred during the char combustion phase, particularly for PB2. Char formation, rather than combustion, was the significant process occurring during the initial stages of these reactions. As previously suggested, BR_I was lower than IR in all cases, thus char remained after volatile combustion. The IFS were similar for all the cases shown, except for the raw switchgrass, due to its very low density (Gilbert et al., 2006). Although the range of IR was vast in previous literature, the results gained were within the range shown in Table 5. The BR was also comparable, except the switchgrass, which showed significantly higher overall BR, although the results for Sp and Sr were very similar. The equivalence ratio at the ignition propagation stage (λ_I) was also calculated. The values for these were significantly lower than those reported in Table 5. The Alkali Index was calculated from the full elemental analyses of the ash samples, assuming that all K and Na present were in oxide form. Probable fouling will occur with the combustion of these pellets. The combustion of the SMC still had the potential to foul, as there were noteworthy amounts of potassium and sodium in the ash.

3.3. Pyrolysis

Three hundred grams of non-pelletised SMC was pyrolysed for 1 h at 500 °C with 2 l/min of nitrogen. The temperature profiles and gas concentrations are shown in Fig. 1. Despite the lack of oxygen in the system, CO_2 was still produced in significant quantities, due to the oxygen present in the feed material. As expected, CO was much higher than combustion, as pyrolysis is a thermal decomposition, not an oxidation, process. In addition to these, other gases were also analysed (Table 6). Towards the end of the reaction, the proportion of hydrocarbon fuels increased, where methane (CH_4), ethane (C_2H_4) and propane (C_3H_8) became more abundant as the temperatures became higher.

In addition to these gases, solid and liquid fuels were produced (Table 7). The char was similar in appearance, in terms of particle size and shape, to the original material, although once pyrolysed, the material became dark and uniform in colour. The liquids separated out, where the heavier, paler pyrolysis liquid settled towards the bottom, with the darker, aqueous phase on top. CV tests revealed large differences between their energy values. The paler pyrolysis liquid had a reasonable CV of 5.85 MJ/kg, whereas the

Table 5
Comparison of quantitative parameters for the combustion in the packed-bed

Test	Parameter								
	ΔM_I (%)	IFS (m/h)	IR (kg/m^{2}h)	BR_I (kg/m^{2}h)	BR_C (kg/m^{2}h)	x BR (kg/m^2 h)	λ_I	AI (kg-alkali/GJ)	ρ (kg/m^3)
PB1	51.4	0.7	296.4	152.5	75.9	109.8	1.27	0.17	442.8
PB2	19.4	1.3	376.8	72.9	120.4	93.7	0.45	0.13	300.3
Mp[a]	75–81	0.36	–	–	–	94–148	2.1–2.3	~0.34	660
Pc[a]	84–86	0.7–0.8	–	–	–	123–134	2.1–2.3	<0.1	272–295
Ww[a]	68–82	1.1–1.2	–	–	–	104–141	2.9–4.1	<0.1	181
RDF[a]	73–75	0.2–0.3	–	–	–	97–112	2.2–2.4	>0.2	715
Cb[b]	68–90	–	190–300	135–310	55–115	–	2.0–2.5	–	76
Sp[c]	90	0.76	280	312	–	252	2.39	–	370
Sr[c]	65.6	8.9	508	385	–	253	2.40	–	57

[a] Ryu et al. (2006).
[b] Ryu et al. (2007a,b).
[c] Gilbert et al. (2006).

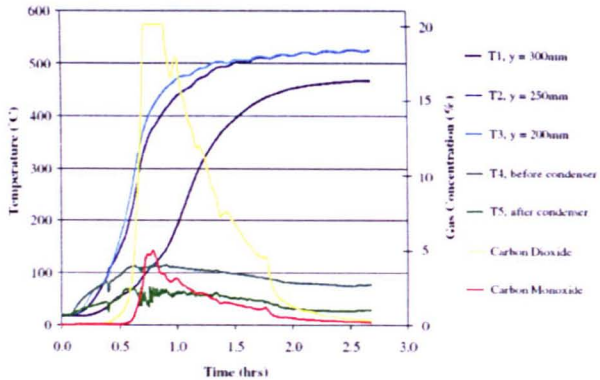

Fig. 1. The temperature profiles and gas concentrations during SMC pyrolysis.

Table 6
Analysis of the changing composition of gaseous fuel products with temperature from SMC pyrolysis

Gas	Gas concentration (%) with temperature			
	350 °C	400 °C	450 °C	500 °C
CO_2	13.02	16.61	14.44	8.19
CO	8.96	9.40	6.67	7.69
CH_4	0.11	0.54	0.78	1.26
H_2	0.04	0.08	0.22	1.34
C_2H_4	0.14	0.08	0.13	0.18
C_3H_{10}	0.06	0.05	0.07	0.08

Table 7
Analysis of the solid and liquid fuel products from SMC pyrolysis

Analysis	Constituent	Char	Liquid
Yield	% g	43.33	34.71
		130	104
Ultimate analysis (%)	Carbon	34.2	5
	Hydrogen	1.2	11.8
	Nitrogen	1.4	1.5
	Oxygen	63.2	81.8
CV (MJ/kg)	GCV	7.95	2.98
	NCV	7.68	-

darker, aqueous phase had a low CV of just 2.16 MJ/kg. The lower CV product was found in greater abundance, however, which was why the overall CV for the liquid phase was low. Separation of these two phases may be beneficial and further processing, as refining may be required.

3.4. Discussion of results

Three technologies were compared, where combustion was most successful and thus deemed the best thermal treatment for SMC and coal tailings, particularly in pellet form. The combustion of both the pellets and SMC were self-sustaining and sufficient temperatures could be generated for the production of useful and moreover saleable heat and/or power. Pellet combustion achieved the greatest efficiency, as the bulk and energy densities were increased by drying and pelletisation, thus pre-processing these wastes is integral to their successful use as a fuel. This was seen particularly in the fluidised-bed, which had the highest overall efficiency. Fluidised-bed combustors usually have higher carbon-burnout efficiencies due to their superior fluid-particle contacting, clearly shown in the comparison between the two combustion methods. Pelletised fuels also generally have better combustion efficiencies than non-pelletised fuels, especially in fluidised-beds where the densified fuel can burn within the bed. The ash produced from pellet combustion has the potential to be utilised as an activator for PFA, eliminating the need for landfilling, as discussed previously (Russell et al., 2005).

The use of SMC-coal tailing pellets clearly has a wide variety of benefits, on the pelletisation of these substances, the combustion process and the overall environmental considerations. The SMC ensures that lower net CO_2 emissions are produced than for conventional fuels, mitigating environmental issues, whereas the coal tailings enhance the CV and thus the energy which can be recovered. Improving the overall CV of the fuel increases the combustion efficiency and the greater bulk and energy densities ensure that combustion takes place within the bed at greater efficiency than the SMC alone. The reuse of both of these wastes also means less land is taken up by landfill sites and coal tailing lagoons; even the ash can be used in an environmental manner.

Pyrolysis did produce a combination of solid, liquid and gaseous fuels and although the CVs of these products were reasonable, they were not necessarily sufficiently high to necessitate the wide-scale use of this technology. Other biomass materials could be used in this process to greater effect. Gasification of the material in a small-scale fixed-bed gasifier was not successful.

4. Conclusions

The main conclusions from this comparison of thermal treatments technologies for the reuse of SMC and coal tailings are as follows:

- SMC-coal tailing pellet combustion in a fluidised-bed was most efficient (91.7%), when compared to packed-bed combustion or the use of unpelletised SMC.
- This produced minimal acid gas emissions (NO_x, SO_x and HCl), although the alkali metal oxide content of the flyash was sufficient to cause possible slagging/fouling in the system.
- Using these wastes for energy recovery provides a sustainable management solution to divert SMC from landfill and aid the reclamation of contaminated land, and is therefore both practical and environmentally-sound.

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Technical Note

Combustion of spent mushroom compost and coal tailing pellets in a fluidised-bed

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ABSTRACT

Previous investigations found that fluidised-bed combustion of spent mushroom compost–coal tailing pellets was preferred for these high ash content fuels. This paper considers the combustion tests carried out on these wastes in a laboratory-scale fluidised-bed, where parameters, including the pellet feedrate, primary/fluidising air flowrate and bed depth, were investigated. Based on the minimum air ratio of 2.5 required to achieve high combustion efficiencies of around 97%, the optimum operating conditions for the combustor employed were a pellet feedrate of 3.25 kg/h (180 kg/m^{2}h) and a total air flowrate of 650 kg/m^{2}h. A lower sand bed depth of 0.22 m was also deemed beneficial, as deeper beds resulted in slugging and noticeable reductions in combustion efficiency. Acid gas emissions (NO_x, SO_x and HCl) were found in limited concentrations, as species remained primarily as inorganic compounds in the flyash. Some N_2O is thought to have formed, as fluidised-bed combustors are particularly prone to this. The alkali index of the ash suggests probable fouling/slagging in the system. For industrial-scale combustion of these wastes, the combustion efficiency could be improved by the presence of secondary air jets to aid turbulent mixing.

1. Introduction

Current fuel sources for energy generation are unsustainable and waste management schemes are environmentally degrading. Consequently, to mitigate the impacts of both these problems, this has led to the development of strategies where wastes are used as fuel resources in thermal treatment processes. The wastes that are investigated herein are spent mushroom compost (SMC), an agricultural waste, and coal tailings, the unwanted substances washed off in coal cleaning processes.

1.1. Spent mushroom compost

SMC is the waste from farms, upon which mushrooms, such as *Agaricus bisporus*, are cultivated. It is composed of two layers: a straw-based substrate with a peat casing layer. The substrate is formed in three stages: (i) pre-wetting where straw, gypsum, horse manure, poultry litter and lime are mixed; (ii) phase 1 composting in windrows and bunkers; and (iii) phase 2 composting involving pasteurisation and conditioning, after which the casing layer is added for spawning, pinning and cropping [1,2]. When the material is nutritionally exhausted, it is 'cooked out' and discarded. As the majority is disposed of in landfill or is reused as an agricultural fertiliser, it is unsustainable and harmful to the environment. Approximately 5 kg of SMC is produced for every 1 kg of mushrooms and the current SMC generation rate in the UK alone is 200,000 tonnes/annum. This lack of sustainable waste management solution is the most significant barrier to the future development and expansion of this industry.

Previous research has been conducted into the use of SMC as a renewable fuel, although there are also many potential agricultural, horticultural and industrial uses. The work on SMC as an energy source has proposed that it can be combusted in a bubbling fluidised-bed to generate power with high efficiency [3–5]. The calorific value (CV) is comparable to other waste fuels currently used, such as municipal solid waste, although drying is required to minimise the high moisture content, which severely reduces the CV. Instead of drying completely, 'auxiliary fuels' like natural gas can be co-fired initially (only during start-up) or continuously to enable greater energy recovery. A demonstration project in Monaghan, Ireland, is seeking to reuse SMC in a combined heat and power station [6]. SMC, poultry litter and possibly wood chips will be used in a spreader stoker boiler or bubbling fluidised-bed to generate 22.5 MW of renewable energy. SMC combustion produces ash, usually about 10% of its original volume, in addition to what it already contains. Russell et al. [7] performed preliminary tests into the reuse of this ash as a chemical activator for pulverised fuel ash in the cement industry, which enhances its pozzolanic reactivity by ensuring rapid early improvements in the strength. This could provide a sustainable disposal method for the ash, thus landfilling would not be necessary. By providing an environmentally responsible waste management strategy for SMC and the ash from combustion, the future of the industry could be secured.

1.2. Coal tailings

Coal tailings are formed when coal is separated from its impurities by cleaning processes and are deposited in lagoons, usually in close proximity to the mining area. Removing coal tailings from these locations will eliminate the risks associated with environmental contamination and lagoon failure.

There are few uses of coal tailings; Noble and Dobrovin-Pennington [8] studied how it can replace some peat in the casing layer of mushroom compost, and Thompson [9] focussed on its reuse for aggregates or for the production of concrete construction blocks. Some have investigated its use as a fuel. Chugh and Patwardhan [10] examined it as an alternative to fuel oils, where the liquid suspension of this could be stored for approximately 3 weeks. Tiwari et al. [11] considered the economic and technical viability of generating mine-mouth power from processed coal tailings, which was found to be feasible on both counts. Through dewatering and capturing the solids, the subsequently obtained fuel was combusted in a bench-scale fluidised-bed, even when the moisture content was high (up to 51%). NO_x, SO_x and mercury emissions were thought to be satisfactorily low. CO release was high, although this could be reduced by employing an industrial burner with a hotter cyclone and increased residence times. Another study considered the formation of fuel pellets from 70,000 tonnes/annum of coal tailings – the waste from the Wallerawang colliery [12]. This is thought to be the greatest potential use of this waste, when combusted with coarse waste from the coal mining industry.

1.3. Previous characterisation and pelletisation of materials

Table 1 shows the material characterisation and elemental analyses performed on the materials. The results were comparable to those previously reported [3,12]. The initial moisture of the coal tailings is around 40%, while that of the SMC is 66%, thus they will require drying prior to pelletisation and certainly before they are used as fuels, since this has severe impacts on the CV. The materials also have a significant ash content. Pelletisation studies showed that a 50:50 SMC:coal tailing wt% ratio was optimal. These results are considered in more detail in previous publications [13,14].

1.4. Preliminary examination of thermal treatment technologies

Preliminary experimentation on recovering energy from these wastes assessed the performance of different thermal treatment technologies (gasification, pyrolysis and combustion in fluidised- and packed-beds) to determine the best option for further investigation [13]. SMC–coal tailing pellet combustion was most efficient, particularly in the fluidised-bed, where the densified fuel burnt within the bed. Moreover, high-ash fuels are better suited to fluidised-bed combustion. Gasification was not successful in the fixed-bed and pyrolysis did not produce fuel products of significant CV. Based on the findings, a further investigation into the fluidised-bed combustion of SMC–coal tailing pellets was undertaken for this study. The aims of this research were to examine, optimise and quantify pellet combustion in the fluidised-bed.

Table 1
Material characterisation and selected results from the full elemental analyses for the coal tailings and the two layers of the SMC on a dry basis

Analysis	Constituent	Coal tailings	SMC substrate	SMC casing
Proximate analysis (%)	Ash	41.25	26.89	28.67
	Volatile	20.51	61.80	60.38
	Fixed carbon	38.24	11.31	10.95
Ultimate analysis (%)	Carbon	47.87	35.13	35.72
	Hydrogen	2.90	3.59	3.01
	Nitrogen	1.01	2.85	1.11
	Chlorine	–	0.51	0.70
	Sulphur	1.38	2.95	2.16
CV (MJ/kg)	GCV (dry)	19.85	14.11	12.37
	GCV (ar)	11.91	4.94	4.33
Elemental analysis (mg/kg)	Al	4360	441.5	1435
	As	14.8	<1	<1
	Ca	2940	40,900	118,500
	Cr	13	3.8	6.2
	Cu	19	46.1	11.7
	Fe	9700	1240	2580
	K	1070	18,650	3685
	Mg	2420	4620	4265
	Mo	2.3	4.1	0.3
	Na	450	2095	600
	P	74.3	6655	4220
	Pb	12.9	2.6	5.1
	Si	1380	1620	1485
	Zn	34.6	194.5	44.1

2. Experimental methodology

2.1. Fuel preparation for combustion tests

The SMC and coal tailings were prepared as for the preliminary experiments. The two raw materials were dried to approximately 10% moisture (from their initially high moistures described above) and mixed thoroughly in a 50:50 wt% ratio prior to compression pelletisation. The materials were not treated in any other way (such as altering the particle size) and no additives, other than the inherent moisture, were used to aid pelletisation. After pelletisation, further drying (to 4–5% moisture) was required to ensure high CV. The 15.5 mm × 12.5 mm pellets formed by this process weighed 1.8 g, on average, and had a bulk density of 496 kg/m^3 after drying.

2.2. Fluidised-bed combustor

The small, laboratory-scale bubbling fluidised-bed used for these experiments consisted of a 1-cm-thick 306 stainless steel 2.3 m × 0.15 m combustion chamber, with a 10-mm-thick stainless steel perforated distributor plate, 200 mm from the base of the reactor (Fig. 1). This plate had nineteen 6-cm-high capped standpipes, each with twenty-seven 1.5-mm diameter holes to evenly distribute the primary air, which acted as both the fluidising and combustion air. The 850-μm diameter medium sphericity sand sat on the distributor plate and formed the fluidised-bed, which was heated using a propane-fired pilot burner; the freeboard above the sand was insulated with a Kaowool blanket. The fuel pellets were fed from the sealed hopper of the calibrated pneumatic screw feeder, along with the secondary air.

2.3. Operating conditions for combustion

Three variables were manipulated: (i) pellet feedrate, (ii) primary (combustion/fluidising) air flowrate and (iii) depth of the fluidised sand bed. A range of values were explored for each, which are shown at the top of Table 2. Case 1 had a moderate air flowrate

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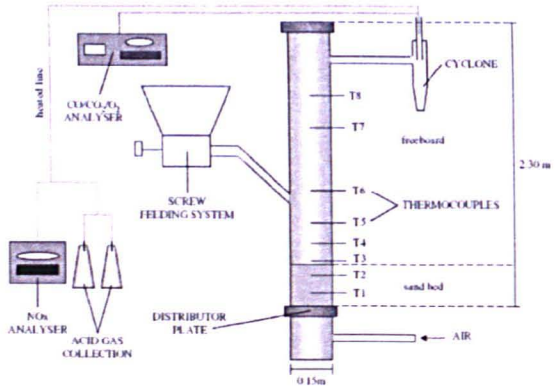

Fig. 1. Schematic of the small, laboratory-scale fluidised-bed combustor.

and a moderate pellet feedrate; other tests were compared to this. Cases 2–6 assessed the impacts of altering the pellet feedrate, ranging from 2.02 to 4.58 kg/h (115–260 kg/m^{2}h), while Cases 7–11 investigated the effects of changing the air flowrate (277–606 kg/m^{2}h). The secondary air was kept almost constant at 170 kg/m^{2}h for comparison. Altering the pellet feedrate and/or the air flowrate changed the fuel-to-air ratio (air ratio) and thus the combustion stoichiometry. All cases used excess air (fuel-lean conditions) and combustion was not attempted with sub-stokhiometric air, as it was thought that the combustion efficiency would be too low and encourage pollutant formation. Lastly, Case 12 looked at the effect of increasing the depth of the sand bed. A wide range of bed depths could not be practically investigated, due to design constrains causing issues with gaining satisfactory fluidisation. Bed depths of 0.22 and 0.27 m were considered (bed depth-to-diameter ratios of 1.47 and 1.8).

2.4. Data analysis

Temperatures throughout the bed and freeboard were monitored using K-type mineral insulated thermocouples (Fig. 1 and Table 3). The exhaust gases passed through the cyclone to remove particulate matter and then entered the online ADC MGA300 gas analyser so O_2, CO_2 and CO concentrations could be recorded, before being discharged to the atmosphere. Based on these, the combustion efficiency (η_{CE}) could be computed by

$$\eta_{CE} = \frac{\%CO_2}{(\%CO_2 + \%CO)}100 \quad (1)$$

where $\%CO_2$ and $\%CO$ are the concentrations of these gases emitted in the exhaust. This is just one of many methods used for calculating the combustion efficiency. Other techniques may take into account various heat fluxes and/or the unburned carbon [15,16]. The unburned material in the ash (remaining combustibles) was assessed separately here.

NO_x (NO and NO_2) were monitored using a Signal Series 4000 NO_x analyser. Chlorides (Cl^-) and sulphates (SO_4^{2-}), which indicate the presence of HCl and SO_x, were collected using a wet chemical method (3% hydrogen peroxide solution with a bromophenol blue ethanol/water indicator) and analysed using gas ion chromatography. From the results, the optimum operating conditions and degree of gas cleaning required were established.

The flyash produced was collected by the cyclone and full elemental analysis by titrations using nitric and hydrochloric acids was subsequently performed. This gave the ash composition, focusing specifically on the metal contaminants. The alkali index, AI – an indicator of potential slagging/fouling – was calculated using the data for alkali metals (K and Na) in the ash:

$$AI = (1/Q)Y_f^a\left(Y_{K_2O}^a + Y_{Na_2O}^a\right) \quad (2)$$

where Q is the gross CV of the fuel on a dry basis (GJ/kg), Y_f^a is the dimensionless mass fraction of ash in the fuel, and $Y_{K_2O}^a$ and $Y_{Na_2O}^a$ are the dimensionless mass fractions of the K_2O and Na_2O in the ash [17]. Other predominant metal species were identified using this technique. The amount of remaining combustible material was also established.

3. Results

The effect of changing these variables was clearly seen on the air ratio, the temperatures achieved and the gas concentrations (and as such, the overall η_{CE}). Tests were repeated to ensure the validity and accuracy of the results, and as such 95% confidence limits are shown as error bars on the graphs to illustrate data variations. The pressure drop, ΔP, across the system was calculated to be 3.44 kPa, using the following:

$$\Delta P = \frac{m}{\rho_p A}(\rho_p - \rho_f)g \quad (3)$$

where m is the mass of the particles (kg), A is the cross-sectional area of the bed (m^2), ρ_p and ρ_f are the density of the particles and the fluidising gas (kg/m^3) and g is the gravitational acceleration (m/s^2).

3.1. Effect of changing the pellet feedrate (Cases 1–6)

The pellet feedrate varied from 2.02 to 4.58 kg/h (115–260 kg/m^{2}h) while other variables remained constant, achieving air ratios between 1.61 and 3.76 (61–276% excess air). The combustion

Table 2
The combustion conditions used for the different cases and the results from the different runs for gas concentrations, combustion efficiency, temperatures and temperature increases

Parameter	Case (run)																							
	1 (1)	1 (2)	1 (3)	2 (1)	3 (1)	3 (2)	4 (1)	4 (2)	5 (1)	5 (2)	6 (1)	7 (1)	7 (2)	8 (1)	8 (2)	9 (1)	10 (1)	11 (1)	12 (1)	12 (2)
Pellet feedrate (kg/h)	3.52	3.52	3.52	2.02	2.46	2.46	2.99	2.99	4.05	4.05	4.58	3.52	3.52	3.52	3.52	3.52	3.52	3.52	3.52	3.52
Primary air (kg/m^{2}h)	415	415	415	415	415	415	415	415	415	415	415	277	277	390	390	468	511	606	415	415
Secondary air (kg/m^{2}h)	155	170	170	170	170	170	170	170	170	170	155	170	170	170	170	170	170	213	170	170
Depth of sand bed (m)	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.27	0.27
Bed depth-to-diameter ratio	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.47	1.8	1.8
Air ratio	2.10	2.16	2.16	3.76	3.08	3.08	2.54	2.54	1.87	1.87	1.61	1.65	1.65	1.84	1.84	2.16	2.51	3.02	2.13	2.13
Average gas concentration																				
CO_2 (%)	12.47	15.29	15.88	4.87	13.40	15.28	15.24	12.99	15.25	16.19	16.39	14.59	17.23	16.95	16.42	16.13	14.90	13.98	15.40	15.67
O_2 (%)	6.22	3.46	2.17	15.37	5.55	4.10	3.20	6.01	2.91	1.98	1.82	3.46	1.00	0.78	0.93	2.89	3.62	4.47	2.06	2.39
CO (%)	0.61	0.53	1.18	0.10	0.38	0.48	0.80	0.43	0.90	0.91	2.47	1.82	1.88	1.94	1.82	0.85	0.83	0.52	1.11	2.03
NO$_x$ (ppm)	1609	805	415	2.09	15.25	23.13	14.63	5.25	7.75	4.34	3.98	58.38	10.42	7.65	2.40			37.88	32.38	36.43
Combustion efficiency (%)	95.34	96.65	93.08	97.98	97.24	96.95	95.61	96.80	94.43	94.68	86.93	88.91	90.16	89.73	90.24	94.99	94.71	96.41	93.28	88.53
Average temperature (°C)																				
Bed	865	876	863	848	825	843	866	860	894	863	887	839	874	865	835	879	862	842	870	865
Above bed	863	876	866	825	825	847	869	861	897	865	892	792	861	854	828	881	861	843	868	866
Freeboard	531	533	450	423	433	484	541	494	567	536	577	387	484	485	414	525	476	502	441	486
Temperature increase (°C/min)																				
Bed	2.63	2.95	2.34	1.26	1.33	2.02	3.23	3.19	3.44	3.90	3.74	1.69	2.87	2.49	1.75	2.96	3.29	3.38	1.68	2.32
Above bed	3.14	3.18	2.37	2.17	1.62	1.98	3.68	3.29	3.62	3.47	3.57	1.90	1.92	2.59	1.95	2.57	3.24	3.67	1.94	2.45
Freeboard	1.37	1.73	2.66	0.98	2.17	0.78	1.23	2.52	1.72	2.06	1.55	2.90	0.66	1.29	1.85	1.65	2.77	3.19	0.60	1.82

Table 3
Locations of the thermocouples within the fluidised-bed reactor

Thermocouple	T1	T2	T3	T4	T5	T6	T7	T8
Height above plate, y (m)	0.11	0.20	0.31	0.42	0.56	0.76	1.54	1.74

conditions and results are shown in Table 2. As the pellet feedrate increased (i.e. the air ratio decreased), the O_2 concentration was reduced and consequently CO_2 increased (Fig. 2). Additionally, CO increased, thus there was more incomplete combustion due to the insufficient air provided. There was also a strong correlation between the η_{CE} and pellet feedrate (Fig. 2). As there was a greater abundance of fuel resulting in diminishing amounts of air available, the η_{CE} decreased rapidly once feedrates above 4 kg/h were reached – air ratios below 1.8. NO_x concentrations were low, but varied from 2.09 to 23.21 ppm.

The temperatures were also significantly influenced by the feedrate (Fig. 3). The temperatures within and just above the bed (T2, y = 0.20 m; T4, y = 0.42 m) were very high, excess of 800 °C in all cases, where the overall temperature increase was around 60 °C between the slowest and fastest feedrates. The effect on the freeboard temperatures (T7, y = 1.54 m) was far more pronounced, where they increased dramatically. The difference between the highest and lowest feedrates exceeded 150 °C and the heating rate was also appreciably affected (Table 2 and Fig. 4). As the feedrate increased, the rate of temperature increase in the bed became more rapid, although the relationship was different for the freeboard. Here, the temperature increase became more rapid as the feedrate increased, until the feedrate was 3.5 kg/h and above this threshold, the rate of temperature change decreased. The temperature increase was also much slower in the freeboard. It is essential to maintain high temperatures to generate energy, thus it is vital to take this into consideration when determining the optimum operating conditions.

3.2. Effect of changing the primary/fluidising air flowrate (Cases 7–11)

The primary air varied from 277 to 606 kg/m^{2}h, achieving air ratios between 1.65 and 3.02 (65–202% excess air), similar to the cases above. The combustion conditions and results are compared in Table 2. Altering the primary air had a less apparent impact on the gas concentrations, even though these were clear for the

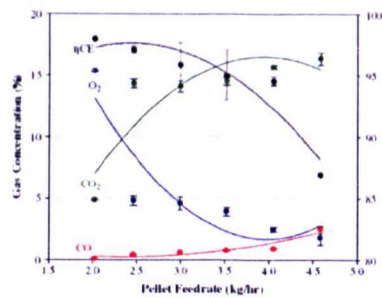

Fig. 2. Trends for increasing pellet feedrates and the gas concentrations in the exhaust and the combustion efficiency.

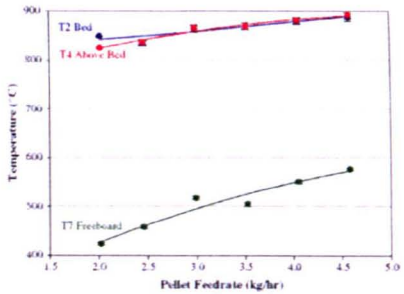

Fig. 3. Trends for increasing pellet feedrates and the temperatures throughout the reactor.

feedrate. The correlation between O_2 and primary air was not as strong as that found with the pellet feedrate (Figs. 2 and 5). The same was also true for CO_2. Whilst some trend was indicated in both cases, these were not as clear as expected with increasing air ratios. The CO correlation was more significant and there was a clear relationship between this and the primary air flowrate. As expected, the incomplete combustion reactions – which produced CO – became less abundant as the air ratio increased. η_{CE} followed a distinct trend, improving considerably with increasing primary air. Again, NO_x varied, but were low and similar to the above tests.

Altering the air flowrate had major implications on the temperatures, which appear as significant as for the variation of the feedrate. This was shown clearly for three main thermocouples (Fig. 6), but the trends were distinctly different than those expressed in Fig. 3, which were fairly linear. Here, the temperatures increased as the air flowrate increased, up to flowrates of 450–475 kg/m^{2}h (air ratios of 2.33–2.43). After this, the excess air in the system became too great and cooled the reaction. As with the pellet feedrate, the bed had the highest temperatures and the freeboard was significantly cooler. The temperatures for all cases were, however, comparable. The rates of temperature increase are shown in Fig. 7. As before, the correlations were significant in all cases, where the freeboard (T7) had the slowest rate and just above the bed (T4) generally had the fastest.

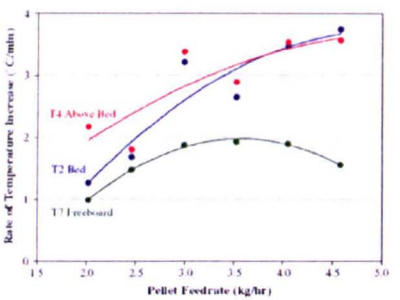

Fig. 4. Trends for the rate of temperature increase with increasing pellet feedrates.

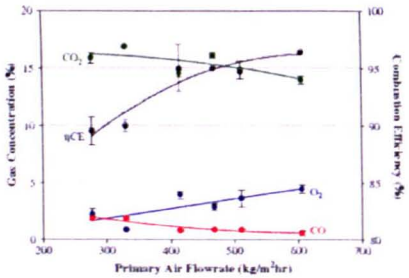

Fig. 5. Trends for increasing primary air flowrates and the gas concentrations in the exhaust and the combustion efficiency.

3.3. Effect of changing the depth of the sand bed (Case 12)

As only two depths were investigated, due to the constraints detailed above, it was difficult to form correlations between the results, although there was some variation in the data for the different depths. The gas concentrations indicated more incomplete combustion for the deeper bed, as CO was more abundant. η_{CE} was thus been reduced from 95 to 90.9% and NO_x were also greater. Although there were large differences in the freeboard temperatures – just over 40 °C with the deeper bed resulting in a cooler freeboard – those in the bed appeared the same. The rates of temperature increase were different but followed the same pattern, with freeboard temperatures rising more slowly. The deeper bed resulted in slower heating rates. Previous attempts at fluidising the bed at 0.30 m were not successful and slugging ensued. The depth-to-diameter ratio of the bed needs to be near to 1 to allow fluidisation to occur effectively. These ratios are shown in Table 2 for the cases here.

3.4. Acid gases and ash analysis

Sulphates and chlorides were captured from the flue gases during combustion to indicate the presence of SO_x and HCl. The

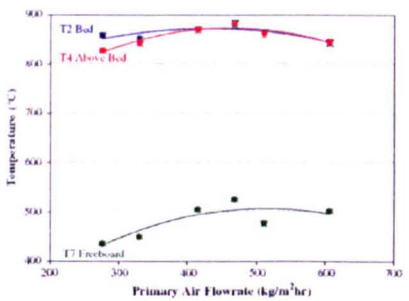

Fig. 6. Trends for increasing primary air flowrates and the temperatures throughout the reactor.

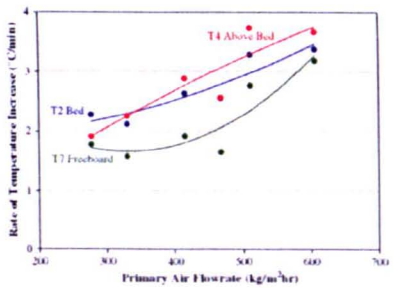

Fig. 7. Trends for the rate of temperature increase with increasing primary air flowrates.

amount of sulphates ranged from 2.35 to 41.69 ppm and the chlorides present ranged from 0.88 to 16.88 ppm (Table 4). These are very low, indicating the SO_x and HCl concentrations were also likely to be minimal, thus little flue gas cleaning will be needed to remove these pollutants. The primary reason for this is likely to be the high concentration of sulphur and chlorine in the ash (Table 5). In addition to these, which were by far the most dominant species, the tests also indicated the presence of metals and other compounds (Table 4). Of these, phosphates, ammonium, nitrates and sodium were the most abundant, but their concentrations were still all low.

NO_x concentrations were found to be low, as predicted by previous literature, and as such, it was thought that the majority of nitrogen would remain as nitrates in the ash, although some was captured in the hydrogen peroxide solution (Table 4). The nitrogen content of the ash, however, was not as high as expected (0.29% compared to 1.76% in the initial fuel), thus nitrogen is probably released as N_2O. Though this is not an acid gas and consequently not classed as a NO_x compound, it is a greenhouse gas and therefore its formation is undesirable.

On average, 80% of the ash in the initial fuel remained as fine particulate ash – flyash, collected by the cyclone. The residual ash in the pellets, along with any that formed on combustion, was either emitted with the flue gases if the particles were too small to be collected or remained in the bed if the particles were large and unable to elutriate. The full elemental analysis looked specifically for sodium and potassium to compute the alkali index; the results from these tests were all highly analogous (Table 5). The AI was between 0.17 and 0.34 kg alkali/GJ, thus fouling is probable, but not

Table 4
Average concentration and standard deviation for pollutant species collected via the wet chemical method and detected using a gas ion chromatograph

Species	Average concentration (ppm)	Standard deviation
Fluoride	0.44	0.71
Chloride	5.33	6.17
Nitrite	0.30	0.15
Bromide	0.60	0.00
Nitrate	3.78	0.86
Phosphate	3.90	3.19
Sulphate	12.03	15.42
Sodium	3.05	1.61
Ammonium	3.53	5.56
Potassium	0.61	0.76
Magnesium	0.22	0.04
Calcium	2.79	3.24

certain. The metals found in the largest quantities were aluminium, calcium, iron and potassium. Other elements, such as sulphur, were also found in large amounts, as considered above. It was also discovered that on average, 13.1% combustible material remained in the ash. Although inefficiencies in the combustor are a likely source, particle carryover, particularly dust formed during pellet feeding, may have also significantly contributed to this. The light SMC particles could have been elutriated by the high air flowrates rather than burn in the bed, before being captured by the cyclone.

4. Discussion

4.1. Air ratio

Both manipulating the air flowrate and the pellet feedrate altered the air ratio, where values between 1.61 and 3.76 were investigated (Fig. 8). This had important ramifications on the nature of pellet combustion and was a crucial factor influencing the exhaust gas composition and thus η_{CE}. Fig. 9 identifies the relationship between the air ratio and gas concentration. The greater the air ratio, the lower the CO, due to the excess air allowing complete rather than incomplete combustion. The relationships for CO_2 and O_2 were even more significant. In addition, the air ratio also had a clear relationship with the η_{CE}. These correlations indicated that the minimum air ratio should be 2.5 for this combustor, so there is sufficient air to ensure high η_{CE} and minimise the formation of detrimental emissions, whilst not allowing excessive amounts of air into the system that cool the reaction. Air ratios lower than this resulted in dramatically lower η_{CE}, whereas higher air ratios did not significantly improve the η_{CE}.

4.2. Pellet feedrate and primary air flowrate

Manipulating the pellet feedrate produced very significant correlations with the temperatures and gas concentrations. The data that indicated high η_{CE}, high temperatures and low pollutant concentrations were gained from the cases where the feedrate was 3.0–3.5 kg/h (170–200 kg/m^{2}h), where the air ratio was 2.2–2.5. This indicated a primary air flowrate in the region of 460 kg/m^{2}h. Compared to the pellet feedrate, the correlations based on the air flowrate were not as significant in some cases, namely, for the CO_2 and O_2, although the relationships with the temperatures and CO were strong. Based on the highest temperature, lowest pollutant concentrations and highest η_{CE}, the optimal primary air flowrate lies within 400–525 kg/m^{2}h, with secondary air at 170 kg/m^{2}h. This suggests that the ideal pellet feedrate will be 3.2 kg/h (180 kg/m^{2}h) for the air ratio to correspond with the value proposed above. The values from the primary air cases correspond well with those for the feedrate cases.

4.3. Depth of the sand bed

As stated previously, it is difficult to form relationships between the variables for the tests concerning the bed depth, as only two cases were compared. There were, however, distinct differences between Cases 1 and 12. The η_{CE} was reduced by the rise in the sand bed, due to the vast increase in CO. Although the bed temperatures were similar, there was a marked reduction in freeboard temperatures, which would inhibit energy recovery. Furthermore, the reactor took longer to heat up as there was more bed material. The depth-to-diameter ratio indicates the likelihood of slugging, where high ratios suggest that slugging is likely. Ratios near 1 are most favourable for achieving proper fluidisation. Here, the combustion chamber is small (diameter of 0.15 m), compared to the bed depths of 0.30 m for the preliminary investigation (depth-to-diameter ratio of 2) [13], 0.22 m for the lower bed depth (ratio of 1.47) and

Table 5
Table showing the cases completed for each of the eight fluidised bed runs and comparing the amount, composition and AI of the flyash collected from each

Component (mg/kg)	Pellets	Average	Ash from run							
			A	B	C	D	E	F	G	H
Test cases	–	–	1, 2, 6	7, 1	10	4, 5, 8, 11	3–5	8, 9	1, 3, 7	12, 12
Flyash as percentage of ash in pellets	–	78.95	65.72	92.08	87.37	74.23	70.22	83.74	84.05	69.22
Alkali index (kg alkali/GJ)	–	0.254	0.239	0.225	0.368	0.220	0.226	0.243	0.248	0.243
Al	2500	45,000	46,000	43,000	45,000	44,000	44,000	48,000	45,000	45,000
As	8	51	62	50	49	54	51	40	50	52
B	14	47.6	50	44	44	45	44	52	49	53
Ba	149	683.8	690	660	680	690	690	730	680	650
Ca	29,680	68,375	67,000	69,000	67,000	68,000	65,000	71,000	75,000	73,000
Cd	0	4.0	5.0	3.0	7.0	4.3	3.9	2.8	2.8	3.0
Cr	3	62	62	62	59	64	64	64	59	62
Cl	–	535	754	–	–	731	636	463	217	406
Co	5	17.4	17	17	17	18	17	18	17	18
Cr	9	52.5	64	46	48	60	52	52	51	47
Cu	29	126.3	130	120	140	120	120	130	130	120
Fe	5604	37,250	40,000	35,000	35,000	41,000	39,000	36,000	37,000	35,000
Ga	–	12.4	13	12	13	13	13	12	12	11
K	8364	20,625	21,000	19,000	21,000	18,000	19,000	22,000	23,000	22,000
La	1	31.9	34	32	31	34	33	30	31	30
Li	6	40.1	33	42	42	40	43	45	43	33
Mg	3485	8325	8000	8600	8200	7700	7900	8900	8800	8500
Mn	196	513.8	580	510	470	550	550	510	480	460
Mo	3	10	10	9.2	11	11	9.8	9.4	9.8	10
Na	1123	3750	4000	3700	3900	3600	3700	3700	3800	3600
Nd	–	26.6	26	26	26	27	27	27	26	28
Ni	13	58.8	65	62	67	66	55	50	56	47
P	3121	5237.5	7100	5100	4200	5600	5600	4800	4800	4700
Pb	8	45	64	41	42	51	50	40	36	36
S	11,702	15,300	13,600	16,100	14,600	14,300	14,500	15,300	16,900	17,100
Sc	1	8.7	8.6	8.3	8.6	8.2	8.5	9.5	9.1	9.1
Si	1487	3137.5	3100	2800	3300	3400	3300	2900	3300	3000
Sr	105	281.9	300	275	275	255	265	280	300	305
Ti	22	502.5	520	390	500	500	480	500	610	520
V	7	78.5	85	72	74	76	73	85	81	88
Y	2	7.9	8.1	7.5	7.8	7.9	7.8	7.9	7.8	8.2
Zn	100	198.8	270	160	210	220	190	180	190	170

0.27 m for the higher bed depth (ratio of 1.8). This will be considered further below.

4.4. Temperatures throughout the reactor and the rate of temperature increase

The maximum temperatures achieved in all cases were in and just above the sand bed, which were both generally above 850 °C (834–887 °C for T2 and 825–892 °C for T4). The temperatures in the freeboard were considerably lower for all cases and also varied much more, between 423 and 577 °C. For the feedrate cases, the temperatures increased in a fairly linear manner; the air flowrate cases also showed a significant trend, where the temperatures increased until a critical value (450–500 kg/m²h) was attained, whereupon the temperatures decreased as the excess air cooled the reaction. As combustion on a commercial scale is used to generate heat and power for energy recovery, the temperatures achieved need to be sufficiently high to be able to create steam to drive a turbine. The temperatures were suitable to generate the heat and/or power required, providing appropriate conditions were used. Furthermore, the combustion reactions were self-sustaining, thus supplementary fuels are not required.

The rate of temperature increase was more rapid in and just above the bed and significantly slower for the freeboard. The reason for this was due to the fact that the fuel was pelletised, and thus dense, so it burned in the bed, rather than in the freeboard.

4.5. Gas concentrations and combustion efficiency

As considered above, there were some significant correlations between the O_2, CO_2 and CO concentrations and the variables manipulated, which were particularly distinct for the feedrate. The relationship between the air flowrate and CO was also significant, although not for CO_2 and O_2. Despite this, a good relationship was still found between the air flowrate and the η_{CE}. As described above, there were conspicuous trends between the air ratio, the concentrations of these gases and η_{CE}. The variation in O_2 was dramatic, and closely matched the air ratio; for extremely air-rich environments, O_2 peaked at over 15%, whereas for less air-rich environments, the concentration was 0.86%. CO_2 also varied noticeably with air ratio (4.87–16.89%). CO was generally low (0.10–2.47%) indicating some incomplete combustion, particularly with less

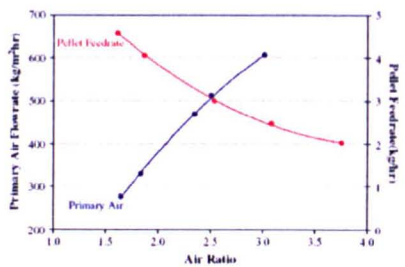

Fig. 8. The relationship between the air ratio and the two dominating influences: the primary air flowrate and the pellet feedrate.

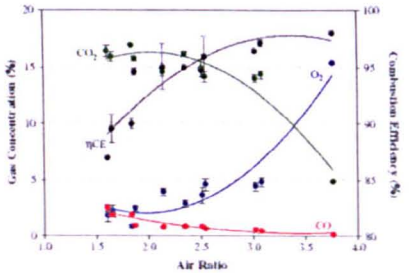

Fig. 9. Correlation between the air ratio and (i) the exhaust gas concentrations and (ii) the combustion efficiency; this combines the results for both the variation of the pellet feedrate and the primary air flowrate.

excess air. The introduction of secondary air injections would further reduce CO.

η_{CE} ranged from 86.93 to 97.98%, where the highest efficiencies were achieved using optimum conditions. It has also been shown that if the conditions are not appropriate, the efficiency is considerably reduced, leading to the formation of pollutants for low air ratios or cooling of the chamber for high air ratios. Although the results indicated that η_{CE} can be high, there were often significant amounts of unburned material in the flyash, as described above. This indicates that a proportion of material is carried over into the cyclone with the exhaust gas and thus the combustion efficiencies were in fact lower than those indicated by the gas concentrations. Furthermore, due to the nature of the small-scale reactor, these efficiencies could be significantly improved by scaling-up the combustor, as considered below, which would improve the combustion efficiency and reduced the amount of material that remains unburned.

4.6. Acid gas emissions

NO_x did not follow a trend or have a relationship with the variables tested or the data collected. The emissions, however, were negligible, which corroborate the results from previous literary sources and the initial investigation [13]. Others identified that NO_x will be minimal if SMC is combusted in a fluidised-bed, due to the inorganic origin (nitrates) of the majority of nitrogen [3,4]. Due to this, expensive NO_x removal systems, such as selective catalytic or non-catalytic reduction, may not be required. As nitrogen was not found to be sufficiently concentrated in the ash, it is likely that N_2O formed instead, although monitoring this was beyond the scope of this work. Fluidised-bed combustors are particularly prone to this, even though NO_x emissions are usually low, as seen here.

Previous literature and the initial investigation also suggested that SO_x and HCl emissions would be minimal if the fuel was combusted in a fluidised-bed, which were confirmed by these findings. Most sulphur should be in inorganic forms (sulphates) and thus negligible SO_x would be formed and although some HCl may arise, most should remain as chlorides in the ash [4]. NO_x and SO_x emissions from coal slurry combustion should also be low [10]. As the Ca content of the fuel is significant (Table 1), due to the lime in the SMC casing, this may also aid the reduction of SO_x, as this is used in lime scrubbing. The large quantities of sulphur and chlorine in the ash explain the low sulphate and chloride concentrations in the exhaust. SO_x and HCl removal, for example flue gas desulphurisation by scrubbing or abatement technologies, will therefore not necessarily be required.

4.7. Ash analysis

Most of the ash in the initial fuel was collected as small particulates using the cyclone attached to the combustor exhaust, thus efficient particulate removal will be essential for large-scale combustion to capture small and sub-micron particles. A fabric filter, for instance, would have a better collection efficiency for this size of particulate material. Many elements were found in considerable concentrations in the flyash, namely, aluminium, calcium, iron, potassium, magnesium, sodium, phosphorus and sulphur, although a range of trace elements were also identified. Through computing the AI from these results, it was found that the alkali metal oxide concentrations were sufficient enough to result in probable slagging/fouling. The AI computed assumed that all the K and Na present in the ash was in oxide form.

5. Optimum operating conditions and industrial implications

From these results, optimum values for the main variables were determined for this combustor, based on an optimal air ratio to ensure efficient combustion. The above discussion of the air ratio suggests that a minimum value of 2.5 should be used; hence at least 150% excess air. Based on this ratio, Table 6 shows the optimum operating conditions for this combustor and the predictions for the gas concentrations and temperatures, from an extrapolation of the experimental results obtained from cases where the bed depth was 0.22 m. The feedrate and air flowrate values both fit within the ideal limits discussed above.

Although these operating conditions apply to the small-scale combustor used, there are industrial implications for the larger-scale combustion of this fuel. The primary one is that appropriately located secondary air jets could improve η_{CE} by aiding circulation so turbulent mixing would redistribute any excess O_2 to enhance the burnout of fuel and residual gases. As described above, large fuel-to-air ratios were required for this small reactor to ensure high η_{CE}, as there was no secondary air circulation. In industry, however, this air ratio could be reduced by additions of high-speed secondary air to optimise fuel–oxidiser mixing; this would reduce the CO concentrations and the combustible material in the ash. Turbulence within the reactor will also help with the avoidance of cold and/or hot spots, which could further limit NO_x formation. Moreover, reducing the air ratio would improve temperature profiles in the reactor, maintaining the high temperatures necessary for energy recovery.

Table 6
The optimum operating conditions (pellet feedrate and primary air flowrate) for an ideal air ratio of 2.6 in this combustor

Parameter	Optimum
Pellet feedrate (kg/m²h)	180
Primary air (kg/m²h)	480
Secondary air (kg/m²h)	170
Depth of sand bed (m)	0.22
Air ratio	2.6
Gas concentration	
CO_2 (%)	14.98
O_2 (%)	3.57
CO (%)	0.60
Combustion efficiency, η_{CE} (%)	96.12
Temperature (°C)	
Bed	865
Above bed	870
Freeboard	519

Predictions for the gas concentrations in the exhaust, upon which the combustion efficiency is based, and the average temperatures in the reactor are given.

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Fuel Pelletization with a Binder: Part I — Identification of a Suitable Binder for Spent Mushroom Compost−Coal Tailing Pellets

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Spent mushroom compost and coal tailings are wastes that could be used as energy sources, through combustion in a fluidized-bed. Our previous pelletization studies produced a denser, yet friable fuel, which produced dust on transport, handling, and feeding. Thus, a suitable binder for these materials was required to enhance pellet properties. Inorganic (caustic soda) and organic (starch) binders were selected for a range of tests. Pelletization at elevated temperatures was also assessed to evaluate the softening of any lignin present in the straw component of the mushroom compost. Small amounts (up to 1 wt %) of both binders increased pellet tensile strength, where starch had more pronounced impacts, doubling the tensile strength to 411 kPa. Pelletization at elevated temperatures (45−75 °C), however, improved overall pellet quality more significantly, increasing the tensile strength to over 600 kPa, although additional temperature increases (up to 125 °C) did not result in further improvements. Whether a binder or elevated temperature is used at the pelletization stage is strongly dependent on the comparative costs of these options, relative to improvements in product quality. The effect of these binders on combustion will also be a crucial factor to consider, which is assessed in the second part of this paper.

1. Introduction

1.1. Pelletization and Binders. Pelletization, the process by which solid particles are consolidated, is employed in many industries to form a more durable substance and to enhance material characteristics. As such, it has a range of purposes: (i) to facilitate storage, transport, and handling; (ii) to combine a number of substances; and (iii) to recycle and/or reclaim materials.[1] When this is related to fuel pelletization, specifically biomass, however, the primary reason is to increase the bulk and energy densities of the material to be somewhat more comparable to that of coal.[2]

If pressure alone does not produce fuel of sufficient quality, binders can be used to improve pellet properties and achieve appropriate fuel standards. Binders have the ability to enhance agglomeration properties and are often added to materials for the purpose of reducing the adversity of pelletization conditions that would otherwise be required. This includes reducing the pressure and/or temperature needed to form good quality pellets. Binding agents are often inherent within fuels, such as lignin in biomass or tar in coal, which are heat-softening. These can be activated with the use of elevated temperatures to improve agglomeration and thus pellet quality, specifically the compressive strength and density.

1.2. Spent Mushroom Compost and Coal Tailings as Fuels. Spent mushroom compost (SMC)—an agricultural waste—and coal tailings, the unwanted substances washed off in coal cleaning processes, have the potential to be combined into fuel pellets and used as an energy source, for example, through combustion in a fluidized-bed.[3,4]

The waste compost from mushroom growing farms is comprised of two layers: a substrate and a casing layer. The substrate is composed primarily of straw, gypsum, horse manure, poultry litter, and lime that are mixed and composted, after which a peat casing layer is added to the surface for mushroom cultivation.[5,6] Once the nutrients have been consumed, the SMC is disposed of in landfill sites or is reused as an agricultural fertilizer, which are both unsustainable and harmful to the environment. The general environmental implications of landfilling waste are well-known. Spreading SMC on agricultural land can have potential detrimental effects on local watercourses, as the phosphorus and nitrates that are common in fertilizers leach into local river networks causing eutrophication[7]—the process whereby nutrients enrich the water, enabling excessive plant growth, in particular, algae, which reduces the dissolved oxygen content of the water, thereby inhibiting the development of fish and other organisms that require oxygen. Furthermore, the generation of SMC far exceeds its demand as a fertilizer, where the current generation rate in the UK is 200 000 tons/annum, approximately 5 kg for every 1 kg of mushrooms.[7] Due to the lack of sustainable waste management solution, this is

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Another industrial implication is the sand bed depth and the depth-to-diameter ratio. Previous literature suggests ratios close to 1 ensure proper fluidisation is achieved. This was clearly substantiated with the lowest ratio here. As such, ratios lower than 1.47 could be used for larger-scale combustors. Furthermore, when the scaling-up of laboratory-scale results is employed to predict the behaviour of industrial-scale combustion plants, it is usually found that combustor performance is improved and the use of a deeper bed (whilst maintaining a low depth-to-diameter ratio) will further improve the efficiency in larger reactors. These results indicate that η_{CE} for these pellets is already quite high, thus optimising the operating conditions of an industrial reactor could ensure the efficiency achieved is increased further.

6. Conclusions

The following conclusions can be drawn from this study into SMC–coal tailing pellet combustion in a laboratory-scale fludised-bed:

- For the combustor employed, the optimum pellet feedrate was 3.0–3.5 kg/h (170–200 kg/m^{2}h) and the most appropriate air flowrate was 400–525 kg/m^{2}h, to ensure an air ratio of at least 2.5 (150% excess air), so high η_{CE} of 97% could be achieved. Lower air ratios could be used for industrial-scale combustion of this fuel, which would ensure high temperatures are maintained.
- A lower bed depth (0.22 m, bed depth-to-diameter ratio of 1.47) produced better results. Scaling-up to a practical-scale plant would mean the depth of the bed could be significantly increased, whilst maintaining a low depth-to-diameter ratio, thus improving the η_{CE}.
- Acid gases (NO_x, SO_x and HCl) were found in limited concentrations, since the majority of these species remain in the ash, thus minimal gas cleaning will be required.
- Particulate collection will be required before the exhaust can be emitted to the atmosphere to capture flyash. The presence of alkali metal oxides is likely to result in fouling/slagging.
- Secondary air jets would increase the fuel and residual gas burnout by turbulent mixing, enhancing the η_{CE} and reducing pollutant formation.

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Appendix A. Abbreviations and nomenclature

A	cross-sectional area of bed (m^2)
AI	alkali index
Cl^-	chlorides
CV	calorific value (MJ/kg)
CWS	coal–water slurry
g	gravitational acceleration (m/s^2)
m	mass of the particles (kg)
NO_x	oxides of nitrogen
Q	the gross CV (GJ/kg)
SMC	spent mushroom compost
SO_x	oxides of sulphur
SO_4^-	sulphates
Y_i^a	dimensionless mass fraction of ash in fuel
$Y_{K_2O}^a$	dimensionless mass fractions of K_2O in ash
$Y_{Na_2O}^a$	dimensionless mass fractions of Na_2O in ash
ΔP	pressure drop (kPa)
η_{CE}	combustion efficiency (%)
ρ_f	density of the fluidising gas (kg/m^3)
ρ_p	density of the particles (kg/m^3)

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Table 1. Table of the Optimum Conditions Used to Form the Best Quality SMC/Coal Tailing Pellets

variable	conditions
initial moisture content	10−11%
drying	fully air-dried
minimum pressure	2500 psi (17.2 MPa)
maximum pressure	6000 psi (41.4 MPa)
holding time	20 s
SMC: coal tailing ratio	50:50

the most significant barrier to the future development of this industry. Reusing the SMC as a fuel, however, could improve the outlook.

The second waste product—coal tailings—is formed when coal is separated from its impurities by crushing, screening, and washing. The ponds and lagoons where it is deposited are usually located in close proximity to the mining area. These have many associated risks, such as environmental contamination and lagoon failure, which necessitate their careful management; removing deposits from these locations and reusing them as a fuel will eliminate these hazards.

The characterization and pelletization of these wastes have been previously considered.[3,8] As the bulk and energy densities of both materials are appreciably lower than for other fuel resources, pelletization is necessary, particularly for use in a fluidized-bed combustor. The materials have significant ash and moisture contents, thus they require drying prior to pelletization and certainly before they are used as fuels, since this has severe impacts on their calorific values (CV). On an industrial scale, the waste heat generated from the use of these fuels can be used for drying the materials; alternatively, a separate drying system could be employed, although this may only be economically viable in larger-scale plants due to economies of scale. The cost of drying fuels, which often constitute a considerable proportion of overall fuel processing costs (particularly those with high moisture contents), depends also on the drying system employed.[9] On the basis of the data from Thek and Obernberger,[8] the drying costs of the coal tailings alone (~40% initial moisture content to 10%) would be in the region of £15/t of pellets, derived from energy consumption costs for a heat price of approximately £19/MWh (from 2006 figures); for SMC (65−70% moisture content, reduced to around 20%), these costs would increase to over £30/t of pellets.[10] The materials in this case were dried naturally in a well-ventilated laboratory prior to pelletization and then fully air-dried after, again without any forced heating.

The pelletization studies of these wastes tested a range of variables, including pressure, moisture, and SMC/coal tailing ratio,[8] from which optimal pelletization conditions were established (Table 1). Although these pellets had considerably greater densities than the initial material, they were friable and produced significant quantities of dust during handling. As such, a binder was required to further enhance their properties, to improve their suitability to feeding via a screw mechanism into a fluidized-bed combustor. As straw is contained within the SMC, it was possible that heating the material could activate any lignin present to act as an inherent binder. The identification of a suitable binder, whether applied or inherent, was the primary aim of this project, achieved through a quantification of improvements to pellet quality. Since these pellets are to be used as a fuel, it was vital that the binder chosen did not detrimentally impact combustion, thus this was also evaluated and is detailed in the subsequent paper.[11]

2. Experimental Procedure and Materials

2.1. Inorganic Binder: Caustic Soda. Caustic soda, also known as anhydrous sodium hydroxide or NaOH, is an inorganic alkali binding agent that has been the focus of pelletization tests, although only one example could be found specifically relating to fuel pelletization. Zhang, et al.[12] examined differing biomass treatments to form a binder for lignite briquettes, where rice straw was treated with a number of chemicals (sulfuric acid, lime, and sodium hydroxide) and was then used as a binder. They found that the type and concentration of chemical was influential; furthermore, the binding method of different chemicals varied, and the temperature and heating were found to be prominent influences. Of the chemicals tested, lime and sodium hydroxide were superior and supplementary additions of bentonite, coal tar and/or polypropylene amide made the pellets more water resistant. Sodium hydroxide was able to bond in both its solid and liquor forms.

Further studies have investigated the pelletization of a range of other materials, including sheep feed[13] and flyash.[14] The results of these investigations showed that only small amounts of the caustic soda binder was required to improve pellet quality, namely pellet strength and hardness. These properties could be further enhanced by using high temperatures.

The caustic soda used for these experiments was in pellet form and required crushing prior to be being mixed with the SMC and coal tailings. The NaOH had a minimum purity of 97.5%, with small amounts of potassium (up to 0.1%) and carbonate (up to 2%) impurities. Care must be taken when handling NaOH, particularly when it comes into contact with moisture, due to it is corrosive nature. It is thus classified as a hazardous chemical.[15]

2.2. Organic Binder: Starch. The second potential binder was starch. This is an organic material, which is often used as a biological binding agent for a variety of purposes; it has pharmaceutical applications and uses in fuel and animal feed pelletization. Here, only literature in the context of biomass fuel pelletization is considered.

Tabil, et al.[16] evaluated the performance of different binders, with the aim of improving the quality of alfalfa pellets, to reduce dust production during transportation and handling. A range of binders were compared: lignosulfonate, bentonite, pea starch, collagen protein, and hydrated lime. All enhanced the durability and hardness of low-quality chop, but did not improve the durability of medium- or high-quality alfalfa. Further testing revealed that just 0.5% of pea starch or hydrated lime could increase pellet durability. Obernberger and Thek[17] tested various densified biomass fuels (pellets for combustion) from across Europe, to investigate pellet quality and European standards for pellet production in this context. The pellet parameters that were analyzed included dimension, density, ash content, gross and net CV, ultimate analysis, and the determination of heavy metals. Additionally, the starch content was established to provide an indication of the inclusion of biological binding agents during pellet production, which was added to aid particle binding, to obtain higher abrasion resistance and to reduce the cost of pelletization. The average starch content was found to be 0.22 wt % for wood pellets on a dry basis, with the maximum at 1.25 wt %. They concluded that biological binders

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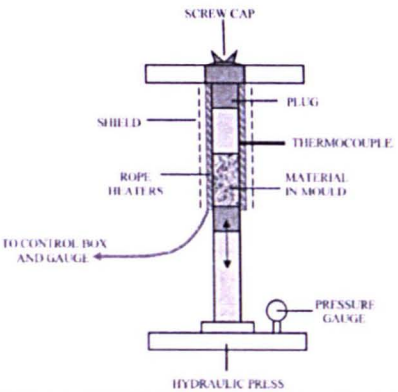

Figure 1. Schematic of the compression pelletizer used to form the pellets.

like starch need only be used in small quantities (up to 2 wt %) in the production of fuel pellets.

A maize-based starch was used for this experimentation. Initially in powder form, it was mixed with a small amount of water (~5 mL per 1.25 g) to form a paste before being incorporated into the SMC−coal tailing mixture.

2.3. Compression Pelletiser. Pellets were manufactured using a compression pelletizer, based on a hydraulic press (Figure 1). 25 g of these wastes were weighed and placed into the 26.8 mm diameter cylindrical mold at the center of the pelletizer. The pressure inside the stainless steel column could reach a maximum of 9338 psi (64.4 MPa). Two 250 W rope heaters (OMEGA FGR-060) surrounded the vertical shaft and were set to specific temperatures, which were monitored using a K-type mineral insulated thermocouple.

2.4. Pelletization with Binders. The use of both caustic soda and starch were assessed as binders for 50:50 wt % SMC-coal tailing pellets. The literature discussed above shows that only a small percentage of these binders are required to impact pellet quality. Various amounts of each binder were added to the mixture prior to pelletization, ranging from 0.5 to 2 wt %. The pellets were made according to the pelletization parameters outlined in Table 1, using the maximum pressure suggested.

2.5. Effect of Temperature. As considered above, elevating the temperature may facilitate the agglomeration of particles, especially if a heat-softening binder has been applied or is inherent to the substance.[18] As SMC is a biomass, composed primarily of straw, lignin and cellulose may be present, which would soften and act as binders if pelletization occurred at elevated temperatures.[19] The rope heaters surrounding the vertical shaft were set to a specific temperature ranging from room temperature (RT = 15 °C) to a maximum of 125 °C, using the control gauge (Figure 1). Pellets of SMC and 50:50 SMC/coal tailing mixtures were made using the same pelletization conditions outlined above.

2.6. Assessment of Pellet Quality. In all cases, pellet quality was determined by assessing pellet density, tensile strength, pellet pile-up studies, and durability, where single factor (one-way) ANOVA tests were performed to assess the statistical significance between results.

The tensile strength (TS, in kPa)—an indicator of cohesion related to pellet size and shape—was calculated from the pellet dimensions and the pellet compressive strength (CS, in N), which was assessed using the Brazilian test. For this, a pellet was placed between the two plates of the Monsanto tensometer and pressure was applied. The maximum radial force that the pellet can withstand was recorded before the pellet failed, by deformation or fracture (breaking/cracking). The radial forces measured here would be lower than the axial forces that pellets of this shape (cylindrical) could withstand. The following equation was employed to convert the values obtained:

$$TS = \frac{2CS}{\pi L d} \quad (1)$$

where L is the pellet length and d is the pellet diameter, both in mm. The data for compressive strength, diameter, length, and density were then manipulated to calculate the maximum height of a pile, relating it to the pressure and weight the pellets can withstand, by employing the following equations. Initially, the overall bulk density of the pellets (ρ_p, in kg/m^3) was required along with d and L; from this, the mean weight per pellet (Wp) in kg was calculated:

$$W_P = \frac{\rho_p L \pi d^2}{4/1\,000\,000} \quad (2)$$

By utilizing Newton's Second Law of Motion, the maximum weight (W, in kg), was computed:

$$W = \frac{CS}{9.8} \quad (3)$$

The number of pellets (P_{No}) in a pile of maximum height that those at the bottom can withstand was thus determined by:

$$P_{No} = \frac{W}{W_P} \quad (4)$$

Using this value and the pellet diameter, the maximum height of the pellet pile (H_p, in m) was calculated:

$$H_p = \frac{P_{No}\, d}{100} \quad (5)$$

The durability of pellets was assessed to determine the most robust and indicated the ability of the pellets to absorb mechanical shocks and withstand abrasion, friction, and vibrations, simulating the conditions experienced during transportation and handling. For each case, five pellets (restricted by drum capacity) were placed in the 100 mm × 200 mm cylinder with a small baffle and mounted into a lathe, which rotated at 40 rpm. The drum was rotated for 20 min—a total of 800 revolutions—and the weight of the pellets that were intact and the larger pieces were measured at 5 min intervals; this was repeated for each case. This is based on the prototype testing method of Temmerman, et al.[20,21] This consisted of a rotating, cylindrical drum containing a baffle, with sieving and weighing the mass at regular intervals. Although there are a range of other testing methods to determine pellet durability, based on the constraints concerning both the project scope (limitations on finances and time scale) and the materials (availability), this was the most suitable technique. Temmerman, et al.[20] explore some of these other methods, including prototype techniques (upon which the method herein was based) and standards tests. ASAE S 269.4 uses a tumbling rectangular ASAE drum with a baffle, whereas ONORM M 7135 incorporates an air stream to swirl the particles

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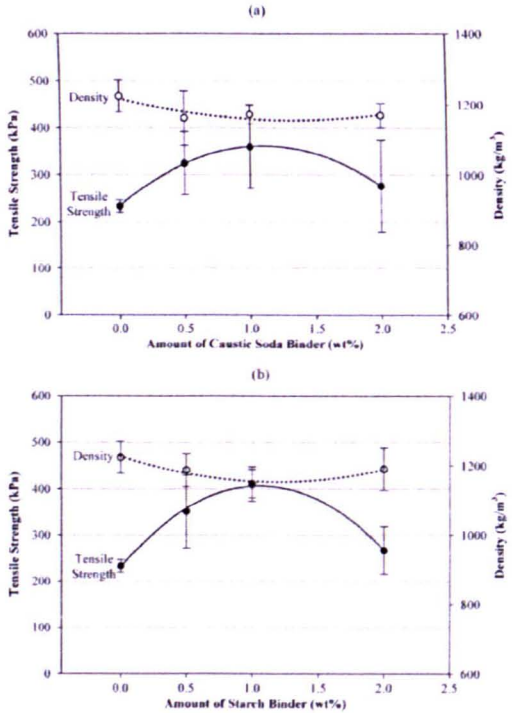

Figure 2. Graph showing the impacts on the tensile strength and density of SMC−coal tailing pellets for (a) the caustic soda binder and (b) the starch binder. The 95% confidence limits are shown as error bars.

within a four-sided pyramidal chamber. In both cases, durability is expressed as the average percentage mass remaining of the total sample. This was thus how the results herein are reported.

3. Results and Discussion

3.1. Comparison of Inorganic and Organic Binders. Up to 1 wt % of both binders improved the tensile strength (an assessment of pellet cohesion relative to size), but further additions weakened the pellets (Figure 2). Opposite trends were seen for the density in both cases. Starch increased the tensile strength more so than the caustic soda. The caustic soda is able to bond to the materials to aid agglomeration and improve pellet quality;[11] however, as seen this is not as effective as the starch binder. Starch, which appears better able to provide this binding function, is thought to assist particle cohesion by solubilization and crystallization within the pellet, in addition to physico-chemical changes through additions of water (~5 mL addition per 1.25 g of starch was used here) and/or heat (as examined below).[22−24]

As seen from the 95% confidence limits in Figure 2, there were noteworthy variations in the results, due to the lack of homogeneity in the materials. Consequently, single-factor ANOVA tests were used to assess the significance in the differences between the conditions; 0, 0.5, and 1.0 wt % of the binders were compared. The only significant difference was found to be for tensile strength, between 0 and 1.0 wt % of starch. Using only a small amount of these binders is beneficial, as quality can be dramatically improved with minimal costs, making these binders economical.

An estimation of the maximum pellet pile height was established using eqs 2−5 (Table 2). Both binders can be used to improve the pellet properties and increase the heights of the pellet piles. Larger improvements were noted with additions of the organic starch binder, compared to the caustic soda. The height of the pellet pile can be increased (considered further below), almost doubled using 1 wt % of starch, without damaging those at the bottom. Based on these results, the optimum percentage of each binder (1 wt %) was chosen and pellets were made to assess their durability. Pellets made with caustic soda were the most durable (with 40.4% mass remaining after 20 min), whereas starch slightly decreased the durability of pellets (31.9%) compared to those without a binder (32.8%).

3.2. Effect of Pelletization at Elevated Temperatures. Pellets made at a range of elevated temperatures were compared to those made under the same conditions at room temperature (15−20 °C). As seen in Figure 3, pellet quality was improved in terms of density and tensile strength with temperature elevations. This was true for both pellet compositions, although it was more pronounced for the SMC, as the largest improvements were seen here. As explored above, it is thought that the lignin and cellulose present in the biomass—in this case, the straw component of the SMC substrate—softens to aid the agglomeration of particles by filling void spaces within the densified pellet, which then cools and solidifies. This is thought to be similar to the effects of tar-binding during the pelletization of coals at elevated temperatures.[25] On the basis of these results, the optimum pelletization temperature is around 75 °C, although vast improvements are seen at just 45 °C, particularly for the SMC, as there would be a larger proportion of lignin and cellulose present.

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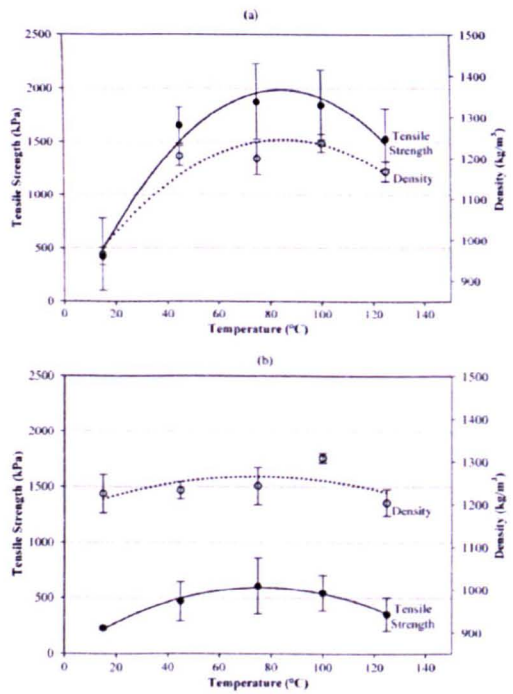

Figure 3. Scatter-plots of the effect of pelletization temperature on the tensile strength and density of (a) SMC pellets and (b) SMC−coal tailing pellets. The 95% confidence limits are shown as error bars.

Table 2. The Maximum Heights of 50:50 SMC−Coal Tailing Pellet Piles Using Caustic Soda and Starch Binders

	binder (%)						
	none	caustic soda			starch		
variables and parameters	0.00	0.50	1.00	2.00	0.50	1.00	2.00
pressure (psi)	6000	6000	6000	6000	6000	6000	6000
pellet length (mm)	33.8	38.7	38.6	39.4	36.4	37.6	36.5
density (kg/m³)	1224	1162	1172	1169	1187	1148	1190
compressive strength (N)	332	531	587	461	540	650	407
weight (kg)	33.9	54.2	59.9	47.0	55.1	66.3	41.5
number of pellets	1449	2139	2347	1811	2262	2725	1693
height of pellet pile (m)	**38.85**	**57.33**	**62.92**	**48.55**	**60.62**	**73.05**	**45.39**

(24) Thomas, M.; van Vliet, T.; van der Poel, A. F. B. *Anim. Feed Sci. Technol.* **1998**, *70*, 59–78.

Table 3. Results for the Maximum Heights of Pellet Piles at Different Pelletization Temperatures, Comparing SMC Pellets and SMC−Coal Tailing Pellets

	pelletization temperature (°C)									
variables and parameters	RT	45	75	100	125	RT	45	75	100	125
pressure (psi)	6000	6000	6000	6000	6000	6000	6000	6000	6000	6000
SMC−coal tailings	100:0	100:0	100:0	100:0	100:0	50:50	50:50	50:50	50:50	50:50
pellet length (mm)	38.1	34.9	37.7	33.8	38.8	33.8	35.9	33.8	33.5	38.2
density (kg/m^3)	965	1195	1200	1238	1168	1224	1232	1243	1308	1204
compressive strength (N)	675	2440	2960	2630	2490	332	710	930	770	575
weight (kg)	69.0	249.0	302.0	268.4	254.1	33.9	72.5	94.9	78.6	58.7
number of pellets	3322	10581	11835	11376	9948	1449	2905	4000	3174	2261
height of pellet pile (m)	**89.0**	**283.6**	**317.2**	**304.9**	**266.6**	**38.9**	**77.9**	**107.2**	**85.1**	**60.6**

The confidence limits in Figure 3 show the variation in the results were large, particularly for the tensile strengths of the SMC pellets, although the averages suggest sizable differences between the temperatures tested; this variation is primarily due to the heterogeneity of the materials. As such, ANOVA tests were completed to assess the statistical differences between the improvements in densities and tensile strengths of pellets made at RT, 45, and 75 °C. Despite the apparent large variation in results, particularly in the tensile strengths, the ANOVA tests indicated there were statistically significant differences between the densities and tensile strengths of SMC pellets made at RT and 45 °C, and also between those made at RT and 75 °C. No difference was found however between those made at 45 and 75 °C, indicating that 45 °C could be used to similar effect, but with incurring fewer costs. The results for SMC−coal tailing pellets showed no statistical differences in the densities or tensile strengths at any temperatures.

The maximum heights of the pellet piles were then computed based on these results (Table 3). As suggested by the tensile strengths and densities, pellets made at elevated temperatures (45 and 75 °C) should be able to withstand significantly higher pellet piles without being damaged. SMC pellets performed consistently better than the mixture of these wastes, particularly at 75 °C, where pellets are thought to be able to withstand pile heights in excess of 300 m. Piles of this magnitude would obviously not be practicable, but indicate that storing these pellets in piles would not be detrimental to their quality. This temperature also considerably increased the pile height for SMC−coal tailing pellets, although not to the same extent. As seen from this table, high tensile strengths are required to stack the pellets, although depending on the type of storage, durability may also be a factor, particularly delivery to the storage facility. There are a range of storage options for such pellets; these include: (i) simple open/covered stores, which are cheap and fuel delivery is straightforward; (ii) underground bunkers, which make fuel delivery easy but are only economic for large-scale systems; (iii) hook-lift bins, which are practical if there is restricted storage space but can cause difficulties with delivery; and (iv) hoppers, which also complicate delivery options and require specific machinery, but are often used when there is limited space available.[25] The use of any of these options would clearly restrict the maximum pellet pile height and thus the optimum height of the fuel pile would be lower than both the maximum pile heights calculated here and the height limited by the storage facility.

Durability experiments compared pellets made at room temperature to those made at the optimum and elevated temperatures, 75 and 125 °C, respectively, for both SMC and SMC−coal tailing mixtures (Table 4). Pellets made at 75 °C were more durable, losing significantly less mass over time,

(25) Jones, D. C. R. *Char Briquettes: An Outline of the Theory and Practice of Manufacture − A Record of the National Coal Board's Research and Development*; National Coal Board.: London, 1969.

Table 4. Durability of SMC and SMC−Coal Tailing Pellets Made at a Range of Temperatures

pellet composition	temp (°C)	durability: % mass remaining
SMC	RT	78.57
	75	93.96
	125	76.25
SMC−coal tailings	RT	32.54
	75	54.85
	125	22.40

for both compositions compared to those made at room temperature. As above, further heating does not produce additional improvements in pellet quality, thus extreme heating (~125 °C) of the materials is disadvantageous, both in terms of pellet quality and energy expenditure (and consequently pelletization costs). SMC pellets were more durable than the mixture, the quality of which was also reflected in the results of the tests above.

These studies demonstrated that pelletization at elevated temperatures (up to 75 °C) was beneficial to pellet quality in terms of density, tensile strength, pellet pile-up, and durability for these materials. At these temperatures, it was thought that any lignin present in the SMC softened and acted as a binder. Increasing the temperature beyond 75 °C, however, did not improve pellet quality further. As lower temperatures are cheaper to maintain, slight temperature increases are convenient in terms of pellet quality and pelletization costs.

3.3. Effect of Pelletization at Elevated Temperatures with a Binder. On the basis of the optimum temperature (75 °C) and an optimum amount of the binders (1 wt %), determined above, tests were carried out to investigate the combination of these, to see if further improvements could be made to pellet quality. The use of the binders coupled with elevated temperatures produced improvements in pellet quality compared to the use of these binders alone, although pelletization using only elevated temperatures was generally superior (Table 5). Durability and density, however, were seen to improve for both binders at 75 °C. ANOVA tests showed that the improvements seen with the use of temperature and the binders (compared to the binders used at room temperature) was only significant for density, not tensile strength.

3.4. Determining the Optimum Pelletization Conditions. On the basis of the results of the previous investigation into pelletization parameters for these wastes and the data gained from the above experiments, the optimum pelletization conditions for SMC and coal tailings can be determined. The addition of 1 wt % of a binder to the SMC−coal tailing mix can further enhance the quality of this fuel, when pellets are manufactured according to the conditions outlined in Table 1. Starch, in particular, improved the tensile strength and pellet pile-up results, the mechanisms of which were explained above, although neither binder improved pellet density. The use of elevated temperatures, even just 45 °C, dramatically improved both the tensile strength and density of pellets significantly,

Table 5. Results for Density, Tensile Strength, Pellet Pile-up and Durability of SMC−Coal Tailing Pellets Made with a Binder at Elevated Temperatures

binder	amount of binder (%)	temp (°C)	density (kg/m^3)	TS (kPa)	max height of pile (m)	durability: % mass remaining
caustic soda	0.0	RT	1224.1	233	38.85	32.79
	1.0	RT	1171.6	360	62.92	40.38
	0.0	75	1242.7	609	107.21	54.85
	1.0	75	1285.7	400	63.64	62.17
starch	0.0	RT	1224.1	233	38.85	32.79
	1.0	RT	1147.5	411	73.05	31.94
	0.0	75	1242.7	609	107.21	54.85
	1.0	75	1296.1	463	72.88	67.57

particularly for the SMC alone−more than the use of these binders. Durability was most improved using a binder at elevated temperatures, although this combination did not further improve pellet tensile strength.

As considered above, high compressive/tensile strengths are required for storing pellets without damaging them, as they are often stacked in large volumes. When the pellets are stored, it is important that the pile heights are lower than the maxima outlined in Tables 2, 3, and 5, to ensure that pellet quality is not compromised, although many of these heights would be improbable for covered storage. Pellet pile height would also be restricted by the storage facility, as considered above. Storage for a lengthy period of time is not recommended, as it can be detrimental to pellet quality, particularly durability.[27] For transportation, handling, and feeding, for example using a screw feeder, durability (tested by resistance to abrasion and mechanical impacts) plays more of an important role. Extensive handling and feeding phases can be detrimental to pellet quality, particularly if pellet durability is not high. This can lead to the formation of dust, which may cause mechanical problems, as well as lead to a reduction in the amount of fuel that can be viably fed into the combustor.

It is vital that the conditions used for pelletization produce appropriate results for both quality assessment criteria (tensile strength and durability) to minimize difficulties with all aspects of storing and using these pellets that may be detrimental to pellet quality. When investigating this for SMC−coal tailing pellets, elevated temperatures (45−75 °C) improved fuel quality the most, in terms of both tensile strength and durability. Despite the superior influences of pelletization at elevated temperatures, the process economics, as explored below, are likely to be the driving factor in the decision making.

3.5. Economics. Adding any preprocessing phase to the utilization of fuels is not economically favorable, although it may be a necessity. The costs associated with pelletization increase with the complexity of the process. Although a simple pelletization operation−for example with no binder or elevated temperatures−is cheap, the best quality pellets are not necessarily formed,[17] as seen herein. These binders are thought to be cost-effective, in that they are cheap to procure and are easy to apply (can be simply combined with the two materials during the mixing phase) while improving pellet qualities, such as tensile strength. On a commercial scale, the cost of 50:50 wt % ratio SMC−coal tailing pellet production (based on capital, consumption, operating−including the dryer and pelletization stages−and maintenance costs) is thought to be about £44/t of pellets excluding transportation costs, increasing to £58/t of pellets with transporting the SMC 200 miles.[10] The cost of drying these materials was examined above. The energy consumption during the pelletization phase of operations is not usually very high, although this does depend on the pressure and complexity of the operation. The specific electricity consumption can vary widely, dependent on plant capacity; for a small-scale wood pellet production facility, it is thought to exceed 150 kW h/t of pellets.[25] What is often the primary factor affecting the overall energy consumption is the degree of drying required−the amount of moisture in the initial materials compared to the most favorable moisture level. Specific heat consumption can be in excess of 1000 kW h/t of pellets, which is predominantly used for drying.[28]

While drying and pelletization seems to already be a costly operation, as the moisture contents for SMC and coal tailings are quite high (65−70% and ~40%, respectively), the use of elevated temperatures in addition to this would considerably increase overall production costs, through greater process complexity resulting in higher capital and operating costs. The extra expenditure used for generating such temperatures could be recovered by utilizing lower pressures, which is a common advantage of pelletization at elevated temperatures. The use of either elevated temperatures or a binder at the pelletization stage is strongly dependent on the comparative costs of these options and the degree of improvement required in product quality.

3.6. Legislation and Policy. There is much legislation in place concerning renewable energy in general, and the use of biomass and biomass wastes specifically. As the SMC portion of the fuel pellets considered here would be classified as a "biomass waste", many of these policies are directly relevant to the use of these fuels. The Renewables Obligation Order, first introduced in 2002, sets targets to licensed energy providers to increase the amount of electricity generated from renewable resources; for 2015−2016, the target is 15.4%. Each MW h of electricity generated from a renewable source results in the issuing of a certificate−a Renewables Obligation Certificate (ROC). Biomass and biomass-derived energy play a significant part, where the incineration and other treatments (including pyrolysis, gasification, and anaerobic digestion) of biomass and biomass wastes, such as the SMC used herein, would be eligible to qualify. Cofiring this with coal tailings, which are fossil-fuel based, would, however, cease to be eligible after 2016. Despite this, the Renewables Obligation coupled with the Climate Change Levy−a support mechanism, whereby renewable energy and CHP are exempt from charges enforced on other energy sources−provides a monetary support mechanism to the renewable energy industry and its development.

Although the SMC alone performed better in the majority of tests, and often exceptionally so, the superior CV of the coal tailings necessitates its use in these pellets. The SMC has a net CV of 13.0 MJ/kg, compared to the coal tailings, which has a

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Fuel Pelletization with a Binder: Part II — The Impacts of Binders on the Combustion of Spent Mushroom Compost–Coal Tailing Pellets

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Various additives, namely, starch and caustic soda, have been identified in the previous paper as binders to improve the quality of fuel pellets made from two wastes—spent mushroom compost and coal tailings. Combustion tests using these pellets in a small, laboratory-scale fluidized-bed were performed to evaluate the impacts these binders had on the efficiency, emissions, and ash properties. Thermal treatment revealed that combustion of these pellets with either binder was fairly comparable to the control case, where no binder was used, in terms of the temperatures achieved and gaseous emission concentrations (including acid gas species). The combustion efficiencies were lower (88.7% compared to 95.0%), possibly due to a modification in particle structure, however there was less combustible material remaining in the flyash. The use of caustic soda increased the likelihood of slagging/fouling within the system, due to the greater concentration of alkali metal oxides in the flyash. The ash fusion temperatures, which also indicate slagging and fouling, were lower for ash containing higher proportions of alkali metals.

1. Introduction

1.1. Pelletization, Binders, and Thermal Treatments. Pelletization is the process by which solid particles are consolidated, using either compression or extrusion, to form a product with more desirable characteristics. If the conditions necessary for pelletization are adverse, a binding agent is often incorporated into the initial material to aid or enhance the agglomeration processes. Although these may have beneficial effects in terms of lowering the pressure required for sufficient compaction or improving pellet quality, in terms of tensile strength or durability, they can also have detrimental impacts.[1] They may degrade the pellet in some way, make them more vulnerable to biological decay, or may produce additional and/or more toxic pollutants if they are used as a fuel, which can be hazardous to both the environment and the equipment employed. As such, any binder that is identified as suitable for improving the quality of fuel pellets needs also to be assessed for any inadvertent influences on their thermal treatment.

Fuels with low bulk densities, such as biomass, are often pelletized to improve the fuel characteristics, as the higher energy density of pelletized fuel directly improves the energy efficiency in a fluidized-bed system.[2] Combustion of fuel pellets in this type of reactor is distinctly advantageous as this allows the densified fuel to burn within the preheated, fluidized bed through using either over-bed or in-bed feeding systems. As the pelletized fuel would have a greater bulk density, it minimizes the number of small and/or light particles that may be carried up through the freeboard with the fluidizing/combustion air and would otherwise escape unburned with the flue gases.[3] Other advantages to fluidized-bed combustion include effective solid–fluid contacting without mechanical components due to the large particle surface area of the bed, good carbon burn-out and high combustion efficiencies can be achieved, and combustion processes are more stable, meaning they can occur at greatly reduced temperatures, which are still sufficient for energy recovery.[4−6] The latter is of particular importance, as this ensures that the occurrence of cold- or hot-spots within the furnace is very much reduced, lowering the excess air requirements, and resulting in significant reductions in pollutants, specifically NO_x and SO_x. Furthermore, fouling, corrosion, and ash fusion are less common. These lower temperatures, however, favor the formation of N_2O; although this is not an acid gas and consequently not classed as a NO_x compound, it is a greenhouse gas and therefore its formation is undesirable.

1.2. Spent Mushroom Compost and Coal Tailings. Spent mushroom compost (SMC) is an agricultural waste from mushroom cultivation, composed of a straw-based substrate and a peat casing layer. Coal tailings are formed when coal is separated from its impurities by cleaning processes. These two wastes have the potential to be combined and reused as fuels, to generate energy from a renewable source. In addition, this will also eliminate the issues concerning the unsustainable disposal of both materials. SMC is primarily disposed of in landfill sites, the negative environmental aspects of which are well-known. Alternatively, it can be used as an agricultural

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considerably greater net CV of 19.2 MJ/kg; its inclusion increases the overall energy content of the pellets to 16.11 MJ/kg. As such, a 50:50 wt % ratio of these is thought to provide a balance of suitable properties, in terms of pellet quality, energy content, and ROC/other renewable energy legislation eligibility.

4. Conclusions

This study compared inorganic and organic binding agents, in addition to the use of elevated temperatures for the formation of high-quality SMC-coal tailing fuel pellets. Up to 1 wt % of the starch binder was more suitable in improving the pellet quality (tensile strength and pellet pile-up) of these wastes, compared to caustic soda. Although the use of elevated temperatures (45−75 °C) with these binders further improved pellet quality, specifically durability, temperature on its own produced more noticeable improvements in tensile strength and density, as the softened lignin aided agglomeration. The comparative costs of these options relative to their improvements will ultimately determine which is employed to enhance the quality for the handling and transporting of these fuel pellets. Future work in this area could address the issues (financial and time) concerning the assessment of pellet durability. A more in-depth investigation into this aspect of pellet quality could provide a comprehensive knowledge of these binding mechanisms.

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Appendix

Acronyms and Nomenclature:
CS = compressive strength (N)
CV = calorific value (MJ/kg)
d = pellet diameter (mm)
H_p = maximum height of the pellet pile (m)
L = pellet length (mm)
$P_{No.}$ = number of pellets in the pile
RT = room temperature
SMC = spent mushroom compost
TS = tensile strength (kPa)
W = maximum total pellet weight (kg)
W_p = mean weight per pellet (kg)
ρ_p = pellet bulk density (kg/m^3)

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Table 1. Averaged Results for the Proximate, Ultimate and Key Results from the Elemental Analyses for the Three Samples and Pellets Composed of a 50:50 SMC−Coal Tailing wt % ratio[a]

analysis	constituent	basis	coal tailings	SMC substrate	SMC casing	50:50 wt % pellets
moisture (%)		ar	~40	65.70	68.56	
proximate analysis (%)	ash	dry	41.25	26.89	28.87	34.27
	fixed carbon		38.24	11.31	10.95	24.74
	volatiles		20.51	61.80	60.18	40.99
ultimate analysis (%)	C	dry	47.87	35.13	35.72	41.56
	H_{tot}		2.90	3.59	3.01	3.19
	N		1.01	2.85	1.11	1.76
	Cl			0.51	0.70	0.27
	S		1.38	2.95	2.16	2.09
	O (difference)		3.69	19.50	20.69	11.65
elemental analysis (mg/kg)	Al	dry	4360	442	1435	2500
	Ca		2940	40900	118500	29680
	Fe		9700	1240	2580	5664
	K		1070	18650	3685	8364
	Na		450	2095	600	1123
	S		4180	23050	3915	11702
	Si		1380	1620	1485	1487
CV (MJ/kg)	GCV	ar	11.91	4.94	4.33	8.36
	GCV	dry	19.85	14.11	12.37	16.81
	NCV	ar	10.55	3.08	2.51	6.76
	NCV	dry	19.22	13.33	11.71	16.11

[a] No binder is included. The CV is also given for each material.

fertilizer, from which phosphorus and nitrates can leach into local watercourses, causing problems such as eutrophication.[7] Coal tailings are deposited in lagoons, from which they can contaminate the environment.

These materials have been characterized (outlined in Table 1) and pelletized to form a more appropriate fuel for combustion.[8−10] Although pelletization under optimum conditions produced a denser fuel, the pellets were friable and created dust when being transported, handled, or fed into the fluidized-bed. Various binding agents were subsequently investigated to improve the quality of this fuel, as detailed in Part I of this paper.[11] It was found that small amounts, up to 1 wt %, of both an organic starch binder and an inorganic caustic soda binder improved pellet quality in terms of compressive strength and pellet pile-up studies. The primary aim of this work was to assess and evaluate the impacts that 1 wt % of these binders have on the combustion of SMC−coal tailing fuel pellets in a small, laboratory-scale fluidized-bed, specifically the overall combustion efficiency, the emissions produced, and properties and composition of the flyash.

2. Experimental Procedure

2.1. Fluidized-bed Combustor. A laboratory-scale bubbling fluidized-bed, shown schematically in Figure 1, was used to combust the SMC−coal tailing pellets. The 1 cm thick 306 stainless steel 2.3 m × 0.15 m combustion chamber has a 10 mm thick stainless steel perforated distributor plate, 200 mm from the base of the reactor. This plate has nineteen 6 cm high capped standpipes, each with twenty-seven 1.5 mm diameter holes to evenly distribute the air through the bed. The medium sphericity sand, which has an average diameter of 850 μm, sat on this distributor plate to form the fluidized-bed, where the freeboard above was insulated with a Kaowool blanket. The chamber was fed with primary air from the compressor through a nozzle distributor in the base, which acted as both the fluidizing and combustion air. The bed was initially heated using a propane-fired pilot burner until the temperatures were stable. Once this was achieved, the fuel was fed in from the sealed hopper of the calibrated pneumatic screw feeding system along with a small amount of secondary air.

2.2. Fuel Preparation and Operating Conditions for Combustion. Three cases were compared to assess the impacts of these additives on the fluidized-bed combustion of the fuel pellets: (i) no binder (control case), (ii) 1 wt % of starch, and (iii) 1 wt % of caustic soda. The materials were dried to ~10% moisture and thoroughly mixed, before a binder, if used, was added. 1 wt % of the starch or caustic soda was included prior to pelletization of these wastes using a compression pelletizer. The caustic soda had a minimum purity of 97.5%. The maize-based starch was mixed with a small amount of water prior to being incorporated into the SMC−coal tailing mix, and the moisture content was then adjusted before pelletization. The 50:50 wt % ratio SMC−coal tailing pellets, the overall material analysis of which is also shown in Table 1, were then allowed to fully air-dry (2−4% moisture) before thermal treatment, to ensure a high pellet CV. These 15.5 × 12.5 mm pellets had a bulk density of 496 kg/m^3, each one weighing approximately 1.8 g.

The combustion conditions utilized were identical for all cases, as seen from Table 2, and each case was repeated between three and five times. Based on the combustion stoichiometry, the amount of theoretical air required for pellet combustion was calculated. For this specific combustor geometry, values for the flow and feedrates were obtained from these calculations. The primary and secondary air flow rates were kept constant at 7.3 kg/h (415 kg/m^2 h) and 2.9 kg/h (165 kg/m^2 h), respectively, and with a pellet feedrate of 3.5 kg/h (200 kg/m^2 h); this resulted in an air ratio of 2.14 (114% excess air). The test runs were completed under fuel-lean conditions—with excess air—to ensure satisfactory combustion efficiencies. The depth of the sand bed was 0.22 m for all cases. These values were experimentally verified through an in-depth investigation into a variety of combustion parameters to optimize fuel burnout in this reactor.[9]

2.3. Data Collection and Analysis. Temperatures, gas concentrations, and ash composition were analyzed for each

(7) Williams, B. C.; McMullan, J. T.; McCahey, S. *Bioresour. Technol.* **2001**, *79*, 227–230.
(8) Finney, K. N.; Ryu, C.; Sharifi, V. N.; Swithenbank, J. *Bioresour. Technol.* **2009**, *100* (1), 310–315.
(9) Finney, K. N.; Sharifi, V. N.; Swithenbank, J. *Renewable Energy* **2009**, *34* (3), 860–868.
(10) Ryu, C.; Finney, K.; Sharifi, V. N.; Swithenbank, J. *Fuel Process. Technol.* **2008**, *89*, 269–275.
(11) Finney, K. N.; Sharifi, V. N.; Swithenbank, J. *Energy Fuels*, http://dx.doi.org/10.1021/ef900020k.

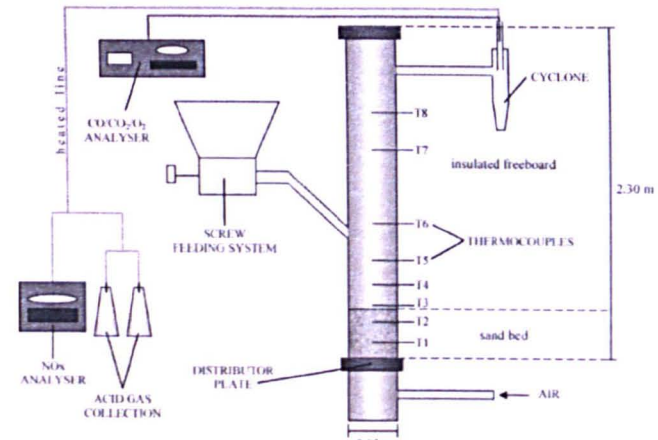

Figure 1. Schematic of the laboratory-scale fluidized-bed combustor.

Table 2. Combustion Conditions and Results from the Tests Assessing the Effects of the Two Binders, Compared to Pellet Combustion without a Binder (Control Case)

		binder		
parameter		no binder	caustic soda	starch
pellet feedrate (kg/h)		3.5	3.5	3.5
primary air (kg/h)		7.3	7.3	7.3
secondary air (kg/h)		2.9	2.9	2.9
depth of sand bed (m)		0.22	0.22	0.22
average gas concentration	CO_2 (%)	14.55	17.25	14.19
	O_2 (%)	3.95	1.40	2.21
	CO (%)	0.77	2.19	1.82
	NO_x (ppm)	23.21	11.81	11.74
combustion efficiency, η_{CE} (%)		95.02	88.73	88.64
average temperature (°C)	bed	869	844	844
	above bed	868	831	837
	freeboard	505	383	461
temperature increase (°C/min)	bed	2.61	2.07	2.60
	above bed	2.89	3.28	3.04
	freeboard	1.92	1.53	1.71

case, according to the experimental setup in Figure 1. The temperatures at eight locations throughout the bed and freeboard were monitored using K-type mineral insulated thermocouples (T1−T8), as indicated in Figure 1. The exhaust gases passed through the cyclone to remove particulate matter and then went to the online ADC MGA300 series multigas analyzer so O_2, CO_2, and CO percentage concentrations could be recorded (on a volumetric basis), before being discharged to the atmosphere. The combustion efficiency (η_{CE}) was derived from these gas concentrations by:[12]

$$\eta_{CE} = \frac{\%CO_2}{(\%CO_2 + \%CO)} \times 100 \qquad (1)$$

where $\%CO_2$ and %CO were the concentrations of these gases emitted in the exhaust. NO and NO_2, collective referred to as NO_x, were monitored in a similar manner, using a Signal Series 4000 NO_x analyzer, which had an error of ±0.2 ppm. Chloride (Cl^-) and sulfate (SO_4^{2-}) species, which indicate the presence of HCl and SO_x, were collected from the exhaust gases using a direct wet chemical method (3% hydrogen peroxide solution with a bromophenol blue ethanol/water indicator) and analyzed using gas ion chromatography, according to British Standard 1756: Part 4.[13] This technique required the exhaust gases (after particulate removal) to be bubbled through the hydrogen peroxide solution, which absorbed any sulfur dioxide by converting it to sulfuric acid. The sulfur dioxide concentration was then determined by gas ion chromatography, which indicated the presence of SO_4^{2-} ions. As gas ion chromatography is able to separate and identify many ions, other species that indicate the presence of pollutants were also categorized, including chlorides for the indication of HCl. The accuracy for this method is within 5%. This test was repeated twice for each liquid sample.

Before the gases were analyzed, the exhaust passed through a 0.1 m diameter and 0.4 m high stainless steel cyclone at the combustor exit to remove any flyash produced during combustion. The remaining gas was discharged to the atmosphere. The particulate matter collected (flyash) underwent full elemental analysis using acid digestion by titrations using nitric and hydrochloric acids. This was followed by ICP-MS (inductively coupled plasma mass spectrometry) detection using a Spectro Cirus ICP atomic emissions spectrometer. This gave the composition of the ash, focusing specifically on the metal contaminants, in particular the alkali, transition, and heavy metal contents, which were then compared to the initial feed material. This test was repeated for each sample of flyash collected.

The combustible material (unburned carbon) remaining in the flyash was experimentally determined, to assess the validity of the combustion efficiencies calculated using the exhaust gas concentrations. This was measured by placing two 1 g samples of the ash into a furnace (at 750 °C) for 1 h.

(12) Llorente, M. J. F.; Cuadrado, R. E. *Fuel* **2007**, *86* (5−6), 867–876.
(13) British Standards Institution. British Standard 1756: Part 4: 1977. *Methods for Sampling and Analysing Flue Gases Part 4: Miscellaneous Analyses*; British Standards Institution: London, 1977.

Lastly, the slagging (deposits within the furnace that are directly exposed to flame radiation, such as the boiler) and fouling (deposits where the cooling of the exhaust gases and flyash particles are not directly exposed to flame radiation) behavior of the flyash was investigated. The Alkali Index (AI) is an indicator of potential slagging and fouling, which was calculated for each case using the elemental composition (data for alkali metals—sodium and potassium) of the flyash:[14]

$$AI = (1/Q)Y_f^a(Y_{K_2O}^a + Y_{Na_2O}^a) \quad (2)$$

where Q is the higher heating value (HHV) of the fuel on a dry basis, in GJ/kg (or the gross calorific value, GCV). Y_f^a is the dimensionless mass fraction of ash in the fuel, and $Y_{K_2O}^a$ and $Y_{Na_2O}^a$ are the dimensionless mass fractions of the K_2O and Na_2O present in the ash, respectively. AI values of less than 0.17 kg-alkali/GJ indicate potential deposition problems, whereas values above 0.34 kg-alkali/GJ suggest fouling is certain; intermediate AI values mean that there is still a probability that slagging and/or fouling will occur. Although a number of indices are available to assess slagging and fouling due to specific components, these are often not appropriate for biomass fuels and, as such, the AI is used here. Although this is thought not to be a comprehensive indicator when it comes to fouling, it is not necessarily an issue, as all biomass fuels tend to exhibit this behavior.[14]

Another measure of problematic deposition occurring within the furnace and boiler of the combustion system is the presence of silicon, aluminum, and iron in their ash in oxide forms,[15] the concentrations of which were determined in the elemental analysis described above. A correlation between the amounts of these oxides present and slag/deposit formation has been found, where Si appears to be the most influential.[15]

The ash fusion temperatures were also determined for each flyash sample by heating a small cone of the ash in a reducing atmosphere (50% hydrogen and 50% carbon dioxide) until it started to melt, according to British Standard 1016: Part 15.[16] Temperatures were determined for the (i) initial deformation, where the edges of the tip of the mound become rounded; (ii) hemispherical stage, where the entire cone becomes hemispherical, such that the height (h_h) is equal to half the base (b) ($h_h = b/2$); and lastly (iii) fluid/flow stage, where the ash has melted and it becomes flat, such that the height (h_f) is equal to a third of height at the hemispherical stage ($h_f = h_h/3$). This can also indicate slagging and fouling, although accuracy can be problematic, as the results often have a high percentage of associated error.[16] This test was repeated twice for each flyash sample.

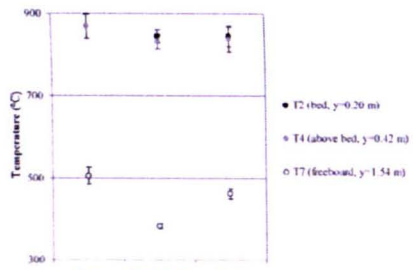

Figure 2. Temperatures (±1SD) during pellet combustion without a binder, compared to pellet combustion with caustic soda and starch binders.

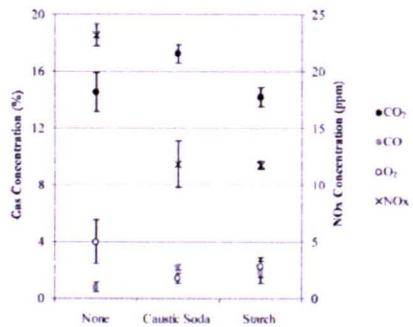

Figure 3. Gas concentrations (±1SD) during pellet combustion without a binder, compared to pellet combustion with caustic soda and starch binders.

3. Results and Discussion

For the control case, where no binder was added to the SMC—coal tailing mixture, the operating conditions resulted in high temperatures toward the bottom of the reactor and high combustion efficiencies (η_{CE}), with low NO_x concentrations, as considered below (Table 2 and Figures 2 and 3). This result and those where a binder was included are compared herein to those of other fuels in similar combustors, as fluidized-beds are used to combust a variety of fossil and renewable fuels. Table 3 compares the operating conditions, emissions, efficiency, and temperatures for several studies. As can be seen, many fuels have been investigated in this context; ranging from fossil fuels, such as various ranks of coal, to industrial and biomass wastes, for example meat and bone meal and olive oil industry residue, as well as energy crops such as sorghum and poplar.

3.1. Temperatures and Excess Air. There were few impacts on the temperatures and the rates of temperature increase, as shown in Table 2 and Figure 2. As with the tests where no

(14) Jenkins, B. M.; Baxter, L. L.; Miles, T. R., Jr.; Miles, T. R. *Fuel Process. Technol.* **1998**, *54*, 17–46.
(15) Öhman, M.; Nordin, A.; Hedman, H.; Jirjis, R. *Biomass Bioenergy.* **2004**, *27*, 597–605.
(16) British Standards Institution. British Standard 1016: Part 15: 1970: *Methods for the Analysis and Testing of Coal and Coke Part 15. Fusibility of Coal Ash and Coke Ash*; British Standards Institution: London, 1970.
(17) Armesto, L.; Bahillo, A.; Veijonen, K.; Cabanillas, A.; Otero, J. *Biomass Bioenergy.* **2002**, *23* (3), 171–179.
(18) Fryda, L.; Panopoulos, K.; Vourliotis, P.; Pavlidou, E.; Kakaras, E. *Fuel.* **2006**, *85* (12–13), 1685–1699.
(19) Henihan, A. M.; Leahy, M. J.; Leahy, J. J.; Cummins, E.; Kelleher, B. P. *Bioresour. Technol.* **2003**, *87* (3), 289–294.
(20) Desroches-Ducarne, E.; Marty, E.; Martin, G.; Delfosse, L. *Fuel.* **1998**, *77* (12), 1311–1315.
(21) Gayan, P.; Adanez, J.; de Diego, L. F.; Garcia-Labiano, F.; Cabanillas, A.; Bahillo, A.; Aho, M.; Veijonen, K. *Fuel.* **2004**, *83* (3), 277–286.
(22) Cummins, E. J.; McDonnell, K. P.; Ward, S. M. *Bioresour. Technol.* **2006**, *97* (7), 903–913.

Table 3. Comparison of Data Concerning the Operating Conditions and Key Results (Emissions, Efficiency and Temperatures) from Various Combustion Studies in Different Types of Fluidized-Bed Reactors

reference	type[a]	fuel(s)	air ratio/ excess air	fluidizing air	emissions	combustion efficiency	temperature
Armesto, et al.[17]	BFB	rice husks	6% excess O_2	1–1.2 m/s	CO: 1194–1808 mg/N m^3; NO_x: 100–430 mg/N m^3	>97%	840 – 880 °C
Fryda, et al.[18]	BFB	meat and bone meal, coal and olive bagasse	1.2–1.6	0.55–1.52 m/s	CO: 100–1150 ppm NO_x: 250–600 ppm SO_2: 250–315 ppm	85.8–99.2%	~875 °C (bed)
Henihan, et al.[19]		poultry litter and peat	5–12% (bed)	1.1–1.3 m/s	CO: 50–400 ppm, NO < 120 ppm, N_2O < 25 ppm	96.3–99.7%	750–850 °C (bed)
Llorente and Cuadrado[12]	BFB	poplar	60–70%				775–850 °C (bed)
Desroches-Ducarne, et al.[20]	CFB	coal and MSW	70% excess air		CO: ~0.87%, NO: 80–160 ppm, SO_2: 20–440 ppm, HCl: 40–420 ppm[b]		800 °C
Gayan, et al.[21]	CFB	coal and pine bark	18–25%	4–6 m/s	CO: 100–400 ppm	96–99.8%	800–900 °C
Cummins, et al.[22]	BFB	peat with meat and bone meal	~6% O_2	96 Nl/min	CO: 24 mg/(N m^3), NO_x: 110 mg/(N m^3), SO_2: 146 mg/(N m^3)		882 °C (bed)
Cubuk and Hesperkan[23]		sweet sorghum and lignite		12 m^3/h	CO: 2730–3480 ppm, NO: 201–222 ppm, SO_2: 62–780 ppm	95.2–95.7%	~850 °C
Armesto, et al.[24]	BFB	olive oil industry residue and coal	6% excess O_2	0.7–1 m/s	CO: 100–180 mg/(N m^3), SO_2: 400–1000 mg/(N m^3)	88–99%	840–870 °C
McIlveen-Wright, et al.[25]	CFB	coal, biomass, and plastic waste	20%		CO: 6019–62.3 mg/(N m^3), NO_x: 345–352 mg/(N m^3), SO_2: 246–257 mg/(N m^3)	net ~38% (based on HHV)	
Huang, et al.[26]	PFB	coal, biomass, and biomass wastes			NO_x: 122–184 mg/(N m^3), SO_2: 125–191 mg/(N m^3), HCl: 85–275 mg/(N m^3)	net ~41–43.5% (based on HHV)	~855 °C (bed)
McIlveen-Wright, et al.[24]	CFB	coal, biomass, and biomass waste			NO_x: 145–280 mg/(N m^3), SO_2: 60–450 mg/(N m^3), HCl: 60–110 mg/(N m^3)	net ~28.2–44% (based on LHV)	480–538 °C

[a] Key: CFB = circulating fluidized-bed; BFB = bubbling fluidized-bed; PFB = pressurized fluidized-bed.

binder was used, the maximum temperatures and the fastest rates of temperature increase were seen in and just above the bed (T2, y = 0.20 m and T4, y = 0.42 m respectively), where combustion was primarily taking place. The bed (T2), however, was slightly cooler for both cases where a binder was used, although the values were still within the standard deviation range (mean ± 1SD) of the control case. The rates of temperature increase were slightly slower within the bed (T2), but elevated just above the bed (T4). The top of the freeboard (T7, y = 1.54 m) was cooler for both binder cases, and for caustic soda in particular. The temperature rise was also slightly slower here, due to the reduction in η_{CE}, as considered below. The temperatures achieved are sufficient for energy recovery, as the temperatures are comparable (toward the high end of the range) to the fludized-bed combustion of other fuels (outlined in Table 3 and discussed below), without necessitating the use of supplementary fuels. Even though the excess air provided to achieve optimum fuel burn-out was high, this did not appear to cool the reactions; however, lowering the air ratio would increase the temperature.

Excess air (fuel-lean conditions) was used here to ensure high carbon burn-outs could be achieved. For the combustion of the SMC—coal tailing pellets, it has been suggested that a large proportion of excess air should be utilized,[9] which is significantly higher that those reported for other fuels in the literature. This is mostly likely due to the small-scale nature and design of the combustor. When these pellets are combusted on a commercial scale, with or without a binder, however, secondary air jets may enhance combustion, for example, by aiding mixing to redistribute excess oxygen, meaning that the primary could be reduced and therefore the amount of excess air could be decreased.

Some of the experiments described in Table 3 used 6% excess oxygen in the system, whereas others used up to 70% excess air or air ratios of up to 1.6. For the cases herein, where the air ratios were 2.14, the excess oxygen present was 2.1% (114% excess air). Even though so much excess air is required to achieve good levels of combustion efficiency, the temperatures achieved, particularly those in the bed, were comparable to those discussed in the literature. The bed temperatures here were generally above 850 °C, which is consistent with the range of 775–900 °C for the studies considered. Many of the papers overviewed in Table 3 report that the temperatures achieved in the freeboard of bubbling fluidized-beds are considerably lower than those of the bed (475–600 °C), which is again similar to the findings of the results here, where freeboard temperatures were generally below 500 °C.[17,18] Henihan, et al.,[19] however, noted that the freeboard temperatures were greater than those in the bed, 930–950 °C, as opposed to 750–850 °C in the bed. Llorente and Cuadrado[12] also reported similar results for a bubbling fluidized-bed.

3.2. Gas Concentrations and Combustion Efficiency. As can be seen, the use of the caustic soda and starch binders did alter the gas concentrations, where there are some differences between these and the control case (Table 2 and Figure 3). The O_2, CO_2, and CO concentrations for the starch case were most comparable to the control, whereas the results for the caustic soda case were less similar. In both instances, there was less O_2, resulting in increased levels of CO_2 and CO. As η_{CE} is based on these gas concentrations, as expressed in eq 1 above, there were also alterations in these values computed for the binder cases compared to the control. The increased amounts of CO for both binder cases resulted in markedly lower efficiencies (88.7% compared to 95.0% for the control). This may be due

Table 4. Average Concentrations for Species Collected via the Wet Chemical Method and Detected Using a Gas Ion Chromatograph; Comparison between the Binders Used

	binder		
average species concentration (ppm)	no binder	caustic soda	starch
chloride	5.33	1.11	2.02
nitrite	0.30	<0.25	
nitrate	3.78	3.70	6.50
sulfate	12.03	9.23	1.98

to an alteration in particle structure within the pellets due to the presence of the binders, or alternatively there is the possibility of additional gas-phase, chemical reactions between the binders and the air, resulting in higher CO and lower O_2 concentrations, reducing the overall η_{CE}. This is also the likely cause for the lower temperatures in the bed compared to the control. As mentioned above, the addition of secondary air jets would be beneficial, by enhancing mixing in the combustor to minimize CO and improve η_{CE}.

Desroches-Ducarne, et al.[20] reported that CO accounted for around 0.87% of flue gas emissions during the circulating fluidized-bed combustion of coal and MSW, which is similar to the control case here. Other research also detail CO emissions, which range quite widely for different fuels; coal cofired with pine bark and peat cofired with meat and bone meal both produced minimal CO emissions in circulating and bubbling fluidized-beds, respectively, whereas rice husks produced more significant concentrations in a bubbling fluidized-bed.[17,21,22]

Furthermore, the combustion efficiency was calculated for many of the investigations reviewed in Table 3; not all, however, were based on the gas concentrations, relating to the carbon combustion efficiency (η_{CE}). The overall net efficiency for the entire system based on either the LHV or the HHV was computed in some cases, which is why these values are particularly low. The η_{CE} value for SMC−coal tailing pellet combustion ranged from 88.7% with the binders to 95.0% for the control case; values reported in the literature had a wider range (85.8−99.8%), although the values herein fit between these limits and therefore correspond well to the efficiencies that can be achieved from the range of other fuels available for this purpose. Llorente and Cuadrado[12] also computed η_{CE} based on the CO and CO_2 gas concentrations, achieving values of 96.3−96.7% for the combustion of poplar in a bubbling fluidized-bed, which is slightly higher than those obtained here for SMC−coal tailing pellet combustion without a binder. Although the efficiency in this combustor can be quite high, due to the small-scale nature of the reactor, these efficiencies could be significantly increased by scaling-up the combustor. In addition, secondary air jets in appropriate locations would increase the residual gas burnout and aid mixing within the system, further enhancing the η_{CE} by reducing the CO present, as more would be oxidized to CO_2. These will be investigated in the future, with the use of a larger, pilot-scale fluidized-bed combustor.

3.3. Acid Gas Emissions. Acid gas concentrations (NO_x, SO_x, and HCl) produced during these tests are reported in Tables 2 and 4. Emission limits for NO_x (NO and NO_2) according to the Waste Incineration Directive, to which the combustion of these wastes must comply, are 200−400 mg/m^3.[23] The daily average for SO_2 is 50 mg/m^3, whereas the half-hourly maximum can be 200 mg/m^3. Legislation concerning HCl emissions, however, is much more stringent, with half-hourly averages being 10−60 mg/m^3, with the daily average set at 10 mg/m^3.

NO_x concentrations varied between 7 and 48 ppm (10.9−74.6 mg/m^3) for all these tests, but the average results for the binder cases were comparable but slightly lower (Figure 3). These average concentrations of 10−20 ppm (15.5−31.0 mg/m^3) are minimal, as predicted by previous literature, and are much below the limits outlined by WID. Others have reported that SMC combusted in a fluidized-bed will produce few NO_x (from the oxidation of fuel nitrogen), SO_x, and HCl emissions, due to the inorganic origin of the majority of nitrogen (nitrates), sulfur (sulfates), and chlorine (chlorides).[7,24] It is also thought that coal tailings should not produce much NO_x or SO_x on combustion.[25] This has subsequently been corroborated by this research herein and by previous investigations.[8,9] Consequently, it was thought that the majority of nitrogen in the fuel (1.76%) would therefore remain in the ash as nitrates, although some was captured in the hydrogen peroxide solution, as shown in Table 4. The nitrogen content of the ash, however, was not as high as expected (0.29%), thus it is probably released as N_2O gas, although measurement of this species is beyond the scope of this project. Fluidized-bed combustors are particularly prone to N_2O formation, as considered above, even though NO_x emissions are usually low. The NO_x emissions that are present are likely to be due to thermal (as air is used instead of oxygen) and prompt (hydrocarbon fragment reacting with nitrogen in fuel-rich areas, due to insufficient mixing) sources. The inclusion of secondary air injections may limit hot/cold spots by encouraging mixing, which could impede prompt NO_x formation.

SO_4^{2-} and Cl^- species were captured using the wet chemical method to indicate the presence of SO_x and HCl. In addition to the sulfates and chlorides, which were by far the most dominant species present, the tests also indicated the presence of other compounds (Table 4). The sulfur content of the initial fuel pellets was around 2.09% (11 702 mg/kg). The amount of sulfates present in the flue gas by comparison were very low, as contemplated below, particularly so when there were additions of starch. This indicates that the SO_x concentration is also likely to be minimal, thus little gas cleaning will be needed to remove these pollutants, as WID outlines a SO_x emission maximum of ~19 ppm. As the Ca content of the fuel is significant (Table 1), due to the lime in the SMC casing layer, this may also aid the reduction of SO_x as this is used in lime scrubbing.[26]

The Cl concentration in the initial fuel was 0.27%. The chlorides present in the flue gas were also low, specifically for the two binder cases, again limiting the need for flue gas cleaning for these species. WID states that the maximum HCl emissions allowed is ~6.7 ppm. The ash analysis, as seen from

(23) DEFRA, Department for Environment, Food and Rural Affairs: Environmental Permitting Guidance - The Directive on the Incineration of Waste, For the Environmental Permitting (England and Wales) Regulations [Online]. Available: http://www.defra.gov.uk/environment/epp/documents/wid-guidance.pdf, 2007.

(24) Williams, B. C. Energy from Spent Mushroom Compost, The Mushroom People, IPP Limited: Wilmslow, UK, 2001; Vol. 3a (120), p 18. [Online]. Available: http://www.engj.ulst.ac.uk/NICERT/mushroom_compost.htm, 2001.

(25) Chugh, Y. P.; Patwardhan, A. *Resour., Conserv. Recycl.* **2004**, *40*, 225–243.

(26) Emre Altun, N.; Hicyilmaz, C.; Suat Bagci, A. *Energy Sources, Part A* **2006**, *28* (5), 469–478.

(27) Cubuk, M. H.; Heperkan, H. A. *Biomass Bioenergy.* **2004**, *27* (3), 277–287.

(28) Armesto, L.; Bahillo, A.; Cabanillas, A.; Veijonen, K.; Otero, J.; Plumed, A.; Salvador, L. *Fuel.* **2003**, *82* (8), 993–1000.

(29) McIlveen-Wright, D. R.; Pinto, F.; Armesto, L.; Caballero, M. A.; Aznar, M. P.; Cabanillas, A.; Huang, Y.; Franco, C.; Gulyurtlu, I.; McMullan, J. T. *Fuel Process. Technol.* **2006**, *87* (9), 793–801.

(30) Huang, Y.; McIlveen-Wright, D.; Rezvani, S.; Wang, Y. D.; Hewitt, N.; Williams, B. C. *Fuel Process. Technol.* **2006**, *87* (10), 927–934.

(31) McIlveen-Wright, D. R.; Huang, Y.; Rezvani, S.; Wang, Y. *Fuel.* **2007**, *86* (14), 2032–2042.

Table 5. Comparison of the Amount, Composition and Alkali Index of the Ash Collected from the Various Cases Compared to the Composition of the Initial Fuel Pellets

	binder			
component (mg/kg)	no binder	caustic soda	starch	initial fuel
flyash as % of ash in pellets	79.0	83.3	75.5	
Alkali Index (kg-alkali/GJ)	0.233	0.293	0.247	
unburned carbon (%)	13.6	12.2	11.7	
Al	44 500	37 250	46 000	2500
Ca	67 750	93 000	92 000	29 680
Cl	560	1050	640	2700
Fe	38 250	29 500	33 000	5604
K	20 250	21 500	27 000	8364
Mg	8275	8250	9900	3485
Na	3775	14 400	4100	1123
P	5650	6250	6800	3121
S	15 225	25 150	27 000	11 702
Si	3150	10 150	7400	1487

Table 5, showed that much of the sulfur and chlorine were contained in the ash/concentrated here rather than in gaseous emissions.

The concentration of NO_x, SO_x, and HCl were also analyzed for many studies, as shown in Table 3, where NO_x and SO_x were often broken down into their component species. The NO_x concentrations for the combustion tests herein correspond well with the results of other literature.[18,19,22,27] In most cases, NO_x emissions from the fluidized-bed combustion of SMC−coal tailing pellets were significantly lower than for other results reported, which generally ranged from 25−250 ppm; the highest value for NO_x species was 650 ppm, from the combustion of a 4:1 lignite/meat and bone meal ratio in a bubbling fluidized-bed with an air ratio of 1.52.[18]

SO_2 emissions were observed for the combustion of meat and bone meal, coal, and olive bagasse in a bubbling fluidized-bed;[18] coal and MSW in a circulating fluidized-bed;[21] peat with meat and bone meal in a bubbling fluidized-bed;[22] sweet sorghum and lignite,[27] olive oil industry residue and coal in a bubbling fluidized-bed;[28] and coal, biomass, and plastic waste in a circulating fluidized-bed.[29] These all report fairly low values, up to 730 ppm for sweet sorghum−lignite blends.[27] Total SO_x were also monitored in some cases, for coal, biomass, and biomass wastes;[30,31] these note low concentrations, as does the combustion of SMC−coal tailing pellets by comparison, as predicted.

Many have monitored HCl emissions for fuel combustion in circulating and pressurized fluidized-beds.[29,30,31] Desroches-Ducarne, et al.[20] suggested that the presence of HCl, even in concentrations as low as 220 ppm, can inhibit CO oxidation, leading to increased concentrations of this species. Huang, et al.[30] found that as Cl in the fuel feed increases, HCl emissions also increase; willow chips, switchgrass, and olive pits, which contained no Cl, produced less than 100 mg/(N m^3) when cofired with coal (0.14% Cl) in 6% excess oxygen, whereas miscanthus and straw, containing 0.25 and 0.28% Cl, respectively, produced 275.8 and 285.5 mg/(N m^3) when cofried in the same ratio. The values obtained here for the combustion of the SMC−coal tailing pellets of 5.33 ppm (~8 mg/m^3)—the maximum amount, for the control case—are significantly lower in comparison, especially when a similar amount of Cl is contained in the fuels compared.

3.4. Flyash Composition and Properties. Flyash samples were collected and analyzed for each case (Table 5). A large proportion of the ash in the initial fuel remains as fine particulate ash, on average 80%, which was collected by the cyclone. The rest, along with any that is formed on combustion, is either emitted with the flue gases, if the particles were too small to be collected by the cyclone, or remain in the bed, if the particles were large and unable to elutriate. Although the treatment of gaseous emissions may not be necessary from the exhaust, it is clear that particulate removal will be required. Smaller particles than those that can be collected by the cyclone employed will need to be removed from the gas stream using a more efficient method for small and submicron particles; a fabric filter, for example, would have a better collection efficiency for this size of particulate.

The composition of the flyash samples are shown in Table 5. This looked specifically for metal contaminants and those found in the largest amounts were aluminum, calcium, iron, and potassium, although other elements, such as sulfur, were also found to be concentrated in the ash, when compared to the initial fuel. These elements appear to be concentrated from the initial fuel pellets into the flyash collected. A range of trace elements were also present. The ash samples from the cases where the binders were included were very similar in terms of composition to the control case. The sodium concentration for the caustic soda case, however, was greatly elevated compared to the control, as discussed below.

These tests also analyzed the concentrations of sodium and potassium, to compute the Alkali Index—an indicator of the potential for slagging/fouling. From the amounts of Na and K established from the elemental analysis, as shown in Table 5, the AI was found to be between 0.17 kg-alkali/GJ and 0.34 kg-alkali/GJ for the case where no binder was used in the combustion of the pellets (Table 5); this indicates that fouling is probable, but not certain. Comparable results were seen for the starch case. Due to the inclusion of the sodium in the caustic soda case, however, the AI of the ash from this test was much greater, as most of this alkali metal was collected in the flyash. Despite this, the value was still within in the limits noted above and did not cross the threshold of 0.34 kg-alkali/GJ into certain fouling. These results suggest that the sodium and potassium concentrations from the fuel pellets alone are sufficient enough to result in the probable slagging and fouling in the system, caused by oxides of these metals. The values obtained for these fuels, even with additions of Na from the caustic soda binder, are equivalent to fuels that are currently used, for example, refuse-derived fuel (RDF), which has an AI value of 0.25 kg-alkali/GJ.[14] Other biomass fuels have considerably greater AI values, such as almond hulls (1.75 kg-alkali/GJ), rice straw (1.65 kg-alkali/GJ), wheat straw (1.1 kg-alkali/GJ), and switchgrass (0.65 kg-alkali/GJ).[14] The AI computed here assumes that all K and Na present in the ash will be in oxide form.

The amounts of Si, Al, and Fe were also ascertained from the elemental analysis and are given in Table 5. As described above, high proportions of these metals in their oxide form can lead to slagging within the combustion system. Although Al and Fe (29 500−46 000 mg/kg) were quite high, Si, which is thought to be more influential, is not so abundant. Critical levels of Si in oxide form (SiO_2) in the ash are thought to be in the region of 20−25 wt %, although the amounts noted here are significantly below this concentration in all cases,[15] even though the Si appears to be concentrated in the flyash. This, coupled with the AI results discussed above, show that slagging and fouling are likely to take place to some extent, simply due to the composition of the SMC and coal tailings, whether the caustic soda binder is included in the feed material or not.

The ash fusion temperatures for the samples, given in Table 6, can also give an indication of slagging and fouling. These showed that, as before, the inclusion of the caustic soda binder

Table 6. Table Showing the Ash Fusion Temperatures of the Flyash Samples

	binder		
ash fusion temperature (°c)	no binder	caustic soda	starch
initial deformation	1160		1191
hemispherical stage	1246	1215	1244
fluid stage	1272	1226	1278

increased the likelihood of inducing these detrimental deposits to form in the combustor, by lowering the temperature at which the ash particles start to deform, melt, and subsequently fuse together. Where starch or no binder was included, the temperatures for ash fusion were much greater; as can be seen, these two cases were similar and there is a greater difference between the hemispherical and fluid stages, unlike with the caustic soda case. The tolerances for these experimentally determined temperatures can be quite high, up to 40 K within the laboratory and up to 80 K between laboratories, thus the differences between the cases may not be as significant as the results indicate.

The unburned carbon content (remaining combustibles) was experimentally determined for each flyash sample (Table 5), where the average was 12.5%. These values are quite high and are fairly constant for each case, resulting from inefficiencies primarily due to combustor limitations. In this case, the primary air may remove small particles, whether they have been combusted or not, hence why the unburned carbon content was similar for each case as the same air flow rates were utilized. This can be used to determine the validity of the combustion efficiency results. The combustion efficiencies calculated from the gas concentrations for the tests where binders were included were significantly lower than when no binder was used. As the amount of unburned carbon in the ash samples from these tests was lower, it may suggest that the overall combustion efficiency was greater than that calculated from these values alone.

4. Conclusions

The combustion of SMC−coal tailing fuel pellets with and without a binding agent was compared using a laboratory-scale fluidized-bed. The temperatures and acid gases emissions were found to be similar for all cases. The increased amounts of CO, however, for the cases where organic starch and inorganic caustic soda binders were included reduced the combustion efficiencies from 95% to around 88.7%. There was slightly less combustible material remaining in the flyash for the cases where binders were used, thus the combustion efficiencies calculated for these may not be as low as the gas concentrations suggest. The emissions of NO_x, SO_2, and HCl are below the limits set out by waste incineration legislation. The inclusion of the caustic soda binder had a detrimental impact on the slagging/fouling behavior of the flyash. When using this combination of fuel and binder, there were larger amounts of alkali metal oxides (sodium) present in the flyash, increasing the probability of deposition within the combustor system, as shown by both the AI and the ash fusion temperatures.

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Abbreviations and Nomenclature:
b = base length of ash cone
CV = calorific value (MJ/kg)
h_f = fluid/flow height of ash cone
h_h = hemispherical height of ash cone
Q = gross CV of the fuel (GJ/kg)
SMC = spent mushroom compost
AI = alkali Index (kg-alkali/GJ)
Y_i^a = mass fraction of ash in the fuel
$Y_{K_2O}^a$ = mass fractions of K_2O in the ash
$Y_{Na_2O}^a$ = mass fractions of Na_2O in the ash
η_{CE} = combustion efficiency (%)

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